TAMPERE UNIVERSITY OF TECHNOLOGY

LIJO GEORGE

MODIFICATION OF FULLERENE WITH ANCHORS

Master of Science Thesis

Examiner: PhD Alexander Efimov
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ABSTRACT

TAMPERE UNIVERSITY OF TECHNOLOGY

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Organic electronics is an emerging field of science which finds application in organic light emitting diode (OLED), organic photovoltaics (OPV), organic transistors, and sensors etc. Research is focused to improve the efficiency of these devices comparable to that of silicon counterpart. Discovery of fullerene has given much greater enhancement to this direction. One of the unique properties of fullerene is that it can reversibly accept up to six electrons. Moreover, fullerene is soluble in common organic solvents, which makes it useful for device fabrication. However, in order to construct functional devices, supramolecular arrangement of molecules on surface is required. Modification of fullerene with anchor ensures patterning of the surface.

Chemistry of fullerenes is described in the Literature Review section citing important reactions such as reduction, nucleophilic substitution and cycloaddition. Methods for synthesis of fullerenes and purifications, details about structure are also described. In addition to that, techniques for supramolecular arrangement of fullerenes on the surface are also given a prominent space under the same section.

Aim of the present work was to synthesize fullerenes with different anchoring groups that can bind on the surfaces covalently and characterize them with spectroscopic methods. We have successfully prepared fullerenes with different anchors such as Mono- and Bis- carboxy, thioacetate, and thiol functional group. The experimental work, interpretation of the spectroscopic data to identify the right compound are presented under Results and Discussion part.

PREFACE

I would like to thank Professor Helge Lemmetyinen for giving me an opportunity to work in the Department of Chemistry and Bioengineering. I am also thankful to Professor Nikolai Tkachenko for directing me to the synthetic chemistry group. I am particularly indebted to Dr. Alexander Efimov for his immense support during my studies and work. He is my supervisor in the research work and has painstakingly reviewed my thesis. He strongly motivated me to accomplish the goals and was kind enough to teach all the spectroscopic instruments used at the synthetic chemistry lab.

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I like to thank my parents, in-laws, siblings and my friends at Biocon Ltd who encouraged me to purse degree from abroad. My warmest thanks go to my wife Simi and our little one 'Lichu' for all the love and support during these years. Above all, I thank almighty God for all his blessings bestowed upon me.

Tampere, August 2014

Lijo George

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ABBREVIATIONS AND NOTATION

OLED	organic light emitting diode
OPV	organic photovoltaics
Alq3	tris (8-hydroxy quinolinato) aluminum
m/z	mass- to-charge ratio
PAH	polyaromatic hydrocarbons
PDBS	poly dibromostyrene
DVB	divinylbenzene
LUMO	lowest unoccupied molecular orbitals
(THA)Br	tetra hexylammonium bromide
THF	tetrahydrofuran
CT complex	charge-transfer complex
TDAE	tetrakis (dimethylamino) ethylene
$CoCp_2$	cobaltocene
DBU	1,8-diazobicylo[5.4.0]undec-7-ene
rt	room temperature
r.m	reaction mixture
LB	Langmuir-Blodgett
SAM	self-assembled monolayer
ITO	indium-tin oxide
DABCO	diazabicyclo [2.2.2]octane
TTF	tetrathiafulvalene
HOPG	highly ordered pyrolytic graphite
BAM	Brewster angle microscopy

Et_3N	triethyl amine
DCM	dichloromethane
TLC	thin layer chromatography
ESI-TOF	electrospray ionization time-of-flight mass spectrometer
J	coupling constant
EtOH	ethanol
TFA	trifluoroacetic acid
DCC	1,3-dicyclohexylcarbodiimide
KSAc	potassium thioacetate
TMS	tetramethylsilane

1 INTRODUCTION

Organic electronics is a relatively new generation of science utilizing the ability of organic molecules to transport the electric charge. It finds tremendous applications in Organic Light Emitting Diode (OLEDs) manufacturing, Organic PhotoVoltaics (OPV), Organic Transistors, Sensors etc. The advantages of organic electronic over silicon based electronics are its unique properties such as flexibility, ability to stretch, softness, sensing capability and biocompatibility. [1] Even though the efficiency of many organic electronic devices, as of now, are low when compared to the inorganic counterparts, the lower cost and high throughput manufacture of devices compensate this deficiency. [8]

The most successful example of practical implementation of organic electronics is OLED. History of OLEDs started with the initial work demonstrated by Prof. Ching.W.Tang and Steven Van Slyke using Alq3 (tris (8-hydroxy quinolinato) Aluminum) in 1987 at Eastman Kodak. OLEDs consist of one or more layers of organic or hybrid molecules sandwiched between anode and cathode. [2] The main benefits of OLEDs on other display systems are that they can produce their light by electroluminescence and do not require any backlight for display and hence are more energy efficient. [1] [3] Furthermore performance of OLED can be enhanced by the inclusion of charge carriers such as fullerenes. [4] Today OLED display technique is widely used for lightings, in display for mobile phones and television and their market share is expected to increase in the near future. The expected trend in the market share for OLED is shown in Figure.1. Corporates companies such as Samsung Display, LG display, Japan Display, AU Optics, BOE Technology Group and Chimei Innolux are key players in the field. [5] [6]

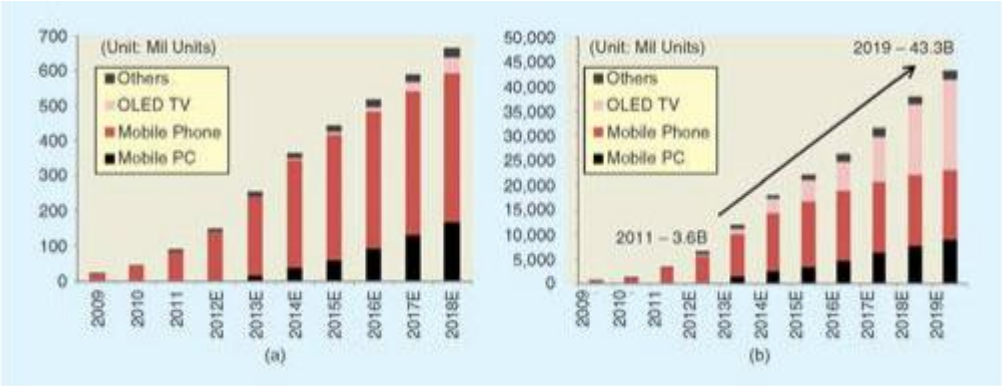


Figure 1.1: OLED market growth forecast for 10years period (a) Shipments (b) Sales [5]

Utilizing sunlight as a source of energy is one of the ways to fulfill the growing energy demand of the world. Organic electronics might provide an exciting near future solution for this demand in the form of OPVs or Organic solar cells. OPVs are semi-transparent, flexible, and roll-to-roll solution processing makes them cost efficient over traditional inorganic solar cells. [9] "Eight19" a UK based company in September 2011, has started providing electricity to the rural areas of southern Africa based on organic solar cell technology. The technology offers clean electricity to people who have no access to traditional on-grid electricity without high purchase costs and at a cheaper rate. [7] The efficiency of OPV depends on the chemical and physical interactions between the materials that harvest light and the materials that transport charge. Research is focused on building interfacial structures that will increase the power conversion efficiency beyond the reported 12 percentage. [1, 8]

The above examples illustrate the dominance of organic electronic industry in the near future, and the role of organic chemists is very high to increase the efficiencies of the devices to a production level. The choice of materials that can efficiently transport charge and the fabrication of these materials onto the devices are important steps in this process. The organic materials used for the organic electronic research include small molecules, polymers and carbon based molecular structures such as fullerenes, nanotubes and graphenes. Carbon based materials hold a special status in organic electronics as they can be rolled, bend, and possess charge storage and conductive ink capacities and can be readily scaled up to an industrial level. [1]

The topic of the thesis work was to synthesize the fullerene based organic charge carrier molecules that can be easily assembled to a device with the help of anchoring groups. Understanding chemistry of fullerene is the basic requirement for the functionalization of the molecule. Details about the structure, preparation, reactivity and immobilization techniques of fullerene will be discussed in the following chapter.

2 FULLERENE CHEMISTRY

Fullerenes belong to the family of carbon allotropes. They are closed polyhedrons made of carbon atoms. The prominent member of the fullerene family is Buckminsterfullerene C_{60} named after famous US architect 'R. Buckminster Fuller', although other clusters such as C_{70}, C_{76}, C_{78}, C_{82}, and C_{84} were isolated and characterized. C_{60} has shape of a truncated icosahedron with 20 hexagons and 12 pentagons. [10] In contrast to other carbon allotropes, fullerenes are soluble in various organic solvents making it useful for chemical modification. [11]

2.1 Numbering

Since the IUPAC nomenclature of fullerenes were too complicated for normal use, according to latest recommendation, Buckminsterfullerene C_{60} was named as (C_{60}-I_h)[5,6]fullerene and C_{70} as (C_{70}-D_{5h})[5,6]fullerene. The parenthetical prefixes indicate the number of carbon atoms, while point group symbol and numbers in bracket give the ring sizes in fullerenes. The numbering of carbon atoms within fullerene is achieved by identification of a well-defined and contiguous helical numbering pathway. [11]

The systematic numbering of fullerenes follows "**Fu-3.1**" numbering system based on set of the rules adapted from CAS publication.

> **"Fu-3.1.1.**Proper rotation axes, (C_n), are examined in sequence, from the highest-order to the lowest-order axis, until at least one contiguous spiral pathway is found that begins in a ring through which a proper rotation axis passes, at the end of a bond bisected by a proper rotation axis, or at an atom through which a proper rotation axis passes. Numbering begins at the end of such a contiguous spiral pathway.
>
> **Fu-3.1.2.**If there is a choice for the selection of a reference axis or for the end of a reference axis to begin the numbering, a ring is preferred to a bond which, in turn is preferred to an atom.
>
> **Fu-3.1.2.1.**When there is a choice between rings; a larger ring is preferred to a smaller one. Where there is still a choice, the preferred ring contains the preferred atom (see Fu-3.1.2.3) at the first point of difference.
>
> **Fu-3.1.2.2.**When there is a choice between bonds, the preferred bond is the common bond between the set of largest rings, for example, 66 > 65 > 55. Where there is still a choice, the preferred bond contains the preferred atom (see Fu-3.1.2.3) at the first point of difference.
>
> **Fu-3.1.2.3.**When there is a choice among atoms, the preferred atom is the common atom in the set of largest rings, for example, 666 > 665 > 655 > 555.

Fu-3.1.3. Where there is a choice of spiral pathways for numbering, the preferred pathway terminates as close as possible, in terms of the number of bonds, to the reference axis of the spiral.**"** [12]

The schematic representations of fullerenes were generally shown either by valence bond (VB) formulas or Schlegel diagram shown in Figure 2.1. Whenever there were a few modifications on parent fullerene molecule or on its derivatives, the widely used representations were VB formulas, and to show each carbon atoms of the fullerene, Schlegel diagram was used. [11]

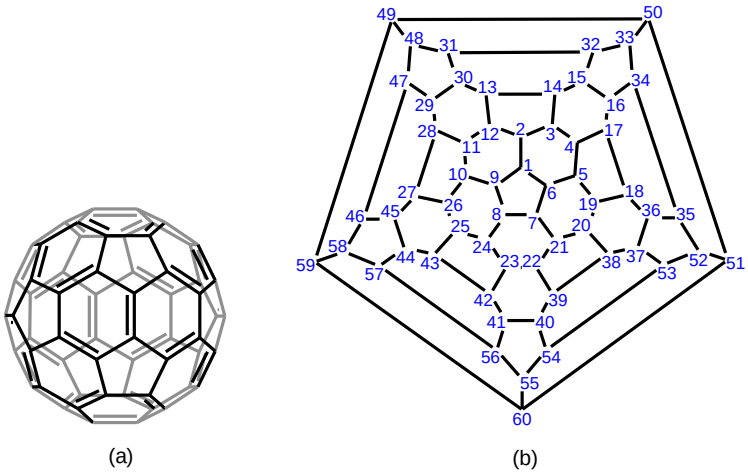


Figure 2.1: Schematic representation of C_{60} (a) VB formula (b) Schlegel diagram with numbering of C-atoms [11]

2.2 Discovery and production

C_{60} was discovered by Harry Kroto (Sussex University), Robert Curl and Richard Smalley (Rice University) in 1985 when they tried to simulate the conditions under which carbon nucleates in the atmospheres of red giant stars by focusing a pulsed laser on graphite in plasma. The mass spectra of these studies under specific clustering conditions were completely dominated by C_{60} signal (720 m/z peak) and to a lesser extent by C_{70} mass peak. [11] However the confirmation of the identity of fullerene by spectroscopic and crystallographic methods as well as by control experiments with ^{13}C enriched material was conducted by Krätschmer and Huffman. They isolated fullerene from the soot generated by vaporization of graphite rods in helium atmosphere, by sublimation or extraction with benzene. Commercially fullerene was produced in macroscopic quantities by any of the following methods. [10] [11]

Production of fullerene by the vaporization of graphite can be achieved either by resistive heating or arc heating. Commercially available "gravity feed generator" developed by Wudl utilizes resistive heating technique for the vaporization. In this reactor, a thin graphite rod (3mm) with a sharpened tip was placed on a thick graphite rod (12mm) guided by a copper sleeve. When a current of 40-60 A was applied, the thin graphite rod evaporated and slipped downward. Once the rod was consumed to a point that it cannot make any electrical contact with the thick rod, the power was shut

off. The yields were about 5-10% based on the evaporated graphite. Other ways of vaporization of graphite were by the use of solar furnaces or inductive heating. [11]

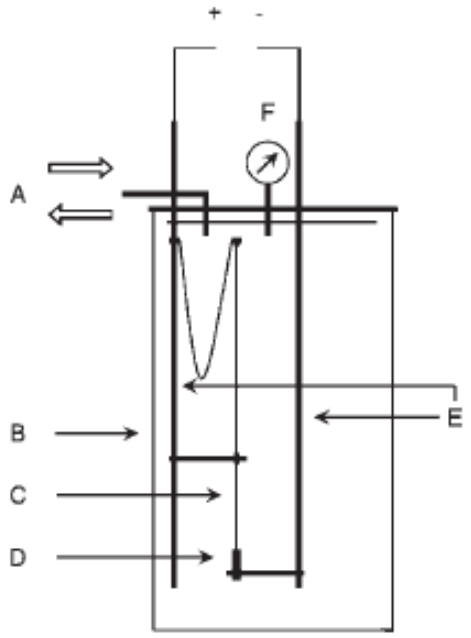


Figure 2.2: Schematic representation of gravity feed fullerene generator. Helium supply and connection to a vacuum system (A), Pyrex bell jar (B), graphite rod (3 mm) (C), graphite rod (12 mm) (D), copper electrode (E), manometer (F). [11]

Fullerene synthesis in combustion was one of the cost efficient methods in production level. In this technology, premixed laminar benzene-oxygen-argon flames operated under various conditions such as pressure, temperature and carbon to oxygen ratios yield fullerenes along with soot and polyaromatic hydrocarbons (PAH). [11]

In addition to these methods, Fullerenes can also be generated by total synthesis approach. Using this approach, specific fullerenes, new endohedral fullerenes, heterofullerenes and other cluster modified fullerenes can be produced, which is not possible by vaporization or graphite combustion of hydrocarbon. [11]

2.3 Structure

C_{60} has shape of a truncated icosahedron with a diameter of 7.1 Å. [10] A truncated icosahedron is derived by replacing the twelve vertices of an icosahedron, each with a five membered ring and each of twenty triangular faces with a six membered ring. [13] Thus sixty sp^2 hybridized carbon atoms of Buckminster fullerene are arranged into 20 hexagons and 12 pentagons. Each pentagon in C_{60} is surrounded with five hexagons and hence it is the smallest possible cage in fullerene family. The presence of pentagons in C_{60} contributes towards its curvature which in turn hinders the delocalization of π-electrons arising from the alternate single and double bond system. [10]

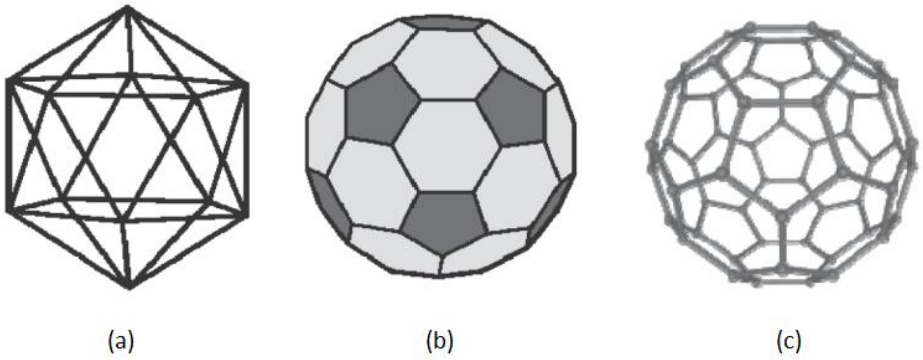


Figure 2.3: a) Icosahedron b) Truncated Icosahedron c) Fullerenes, [13]

2.4 Isolation and purification

The evaporation of graphite produces soot and slag which contain mixture of soluble fullerenes and other kinds of closed carbon structures such as giant fullerenes (Carbon number greater than 100) and nanotubes. Hence in order to isolate fullerenes from the mixture, either sublimation or extraction was employed. [11]

Normally gradient sublimation of soot ensures a partial separation or enrichment of different fullerenes which were deposited on a quartz rod along a temperature gradient. Even though the method leads to the partial decomposition of fullerenes by thermal stress, it was used for the enrichment of C_{74} which was not obtained by the extraction of soot. [11]

Extraction with organic solvents was the common method for isolating fullerenes from the soot. Toluene was the preferred solvent owing to its sufficient solubility for fullerenes and less toxicity while other solvents such as hexane and heptane were also used. High yield of fullerene can be obtained by Soxhlet extraction of the soot. [11]

Purification of fullerenes from the fraction was achieved by chromatographic techniques. Column chromatography with alumina as a stationary phase with either hexane or hexane-toluene mixture (95:5) as eluent yields C_{60} as the first fraction. The efficiency of purification of fullerenes can be improved by using modified Soxhlet chromatography apparatus as shown in Figure 2.4. The advantage of this method was that it did not require large quantities of solvent or constant monitoring. [14]

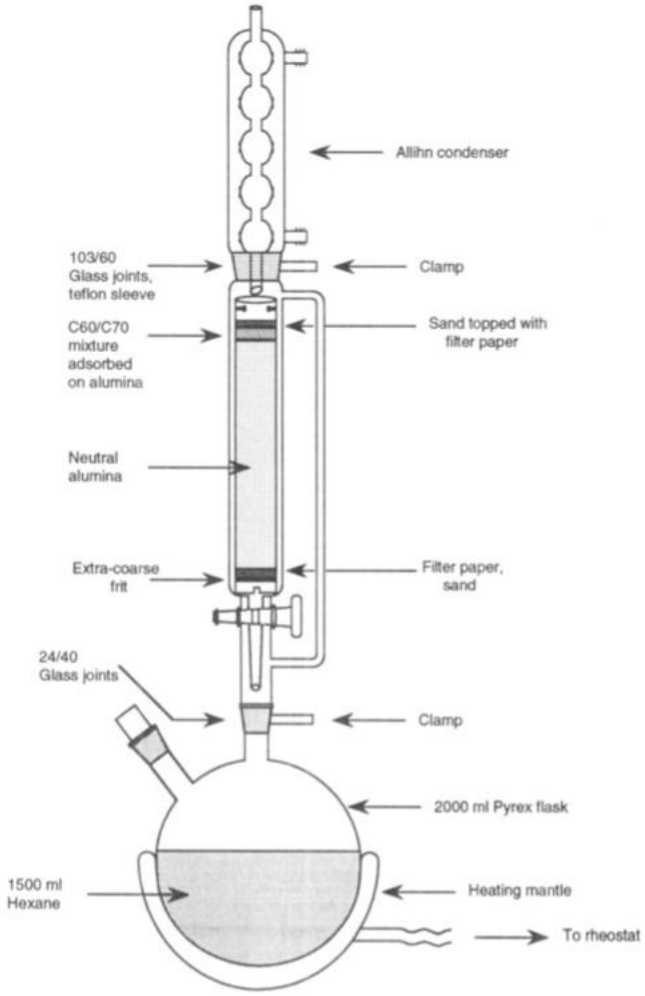


Figure 2.4: Schematic representation of the modified Soxhlet chromatography apparatus. [14]

Other inexpensive and efficient methods were either use of a flash column with a mixture of charcoal and silica gel or filtration through a thin layer of activated carbon using toluene or chlorobenzene as eluent. [11]However, for the separation of higher fullerenes (above C70) from the crude fullerene mixture, polystyrene gel as stationary phase and toluene as mobile phase were used. By using poly (dibromostyrene)/divinylbenzene(PDBS/DVB) as a stationary phase and chlorobenzene as a mobile phase, preparative amounts of C_{60}, C_{70} and higher fullerenes from crude fullerene mixture were enriched in a single elution. [15] HPLC methods using C18-reversed phase silica were useful for analytical purposes or were efficient for separation of higher fullerenes and fullerene derivatives containing covalently bound groups. The protocol for fullerene separation and isolation is shown in Figure 2.5 [11]

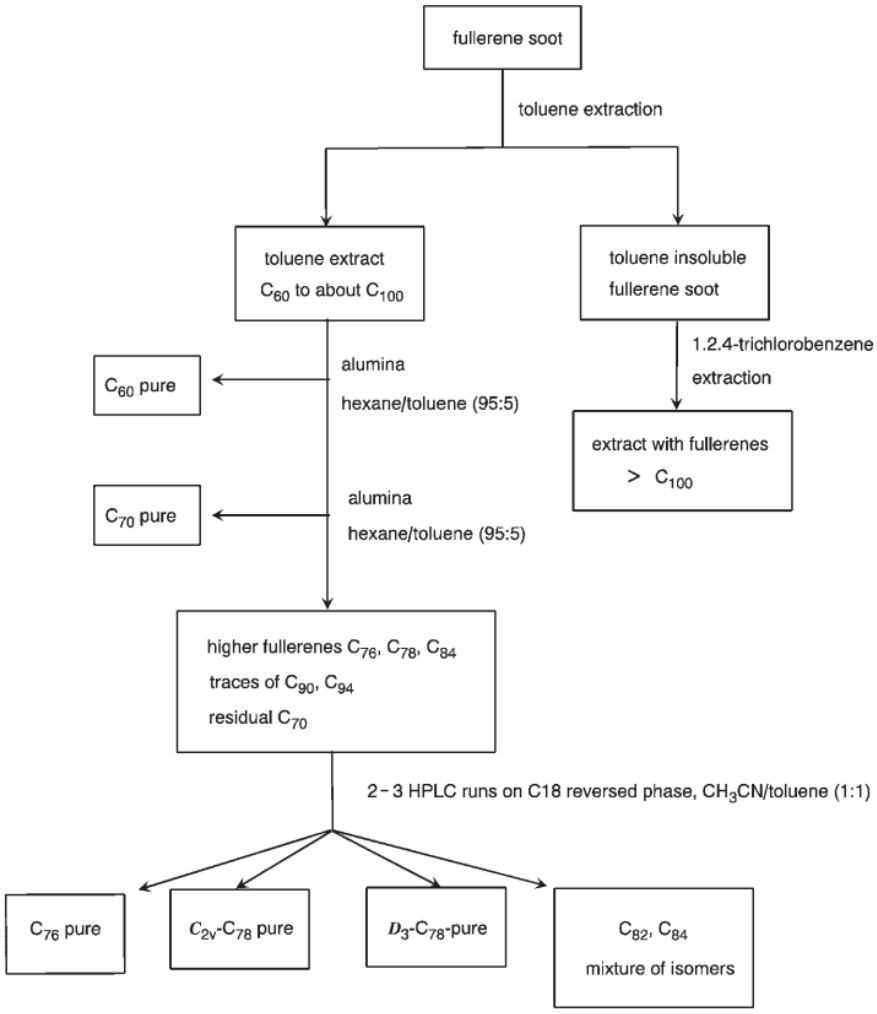


Figure 2.5: Protocol for fullerene separation and isolation [10]

Another way to separate C_{60} from a mixture of C_{70} was to utilize the slight difference in chemical reactivity. C_{70} readily react with $AlCl_3$ in carbon disulphide to form $C_{70}[AlCl_3]_n$ and can be separated from CS_2 as precipitate. [11] C_{60} with purity up to 99.99% can be obtained by triple fractional crystallization from 1,3-diphenylacetone and subsequent charcoal filtration. [16]

2.5 Chemistry of fullerenes

Fullerene is unique among the carbon allotropes due to its solubility in organic solvents, closed cage structure, crystal lattices and its distinctive physical properties. The chemistry of fullerenes can be broadly classified in two types. First is *Exohedral* derivatization, i.e., chemical modification of the outer surface of the cage under various reaction conditions and second is *Endohedral* (Incar) complexes, i.e. trapping atoms within the fullerene cage. [18]

The ^{13}C NMR spectrum of C_{60} shows a single signal which can be attributed to sixty equivalent sp^2 carbon atoms. [18] However the curvature of the fullerene induces slight mix-up of sp^3 character. The chemical reactivity of C_{60} can be understood by viewing the molecule as a non-overlapping, octahedral arrangement of six pyracyclene units with four arranged at the belt and two units on the top and bottom. Each pyracyclene unit (Figure 2.6) consists of two pentagons and two hexagons and a central (reactive) double bond. Thus in the remaining eight hexagons four are isolated from each other by pyracyclene units. [17]

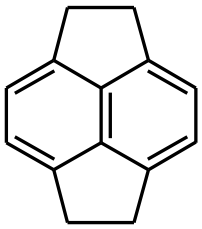


Figure 2.6: Representation of pyracyclene unit in C_{60} [16]

Fullerene consists of two types of bonds; long bonds (0.145 nm) at the junction of five- and six-membered ring called as [5, 6] bonds and shorter bond (0.139 nm) at the junction of two six-membered rings called as [6, 6] bonds with double bonds character are shown in Figure 2.7. [18]The single bonds present in pentagons prevent the delocalization of π electrons and hence fullerene behaves as an electron-poor conjugated polyolefin rather than an aromatic molecule. [17] The addition of groups with less steric requirements, such as hydrogen, prefer 1,2-addition across [6, 6] bond (Figure 2.7 b) and groups with significant steric requirement prefer 1,4 addition (Figure 2.7c) with a relocation of a double bond into the pentane ring. Cycloaddition reactions (Figure 2.7 d) normally happen at adjacent carbon atoms of [6, 6] double bond with lesser extend at [5, 6] bonds. [18] The presence of 30 equivalent double bonds in the molecule make fullerene least selective to the chemical reactions. [17] The regioselectivity of polyaddition can be achieved by using either template- or tether-directed synthetic approaches. In the template-directed method, the reversibility of certain reactions such as Diels- Alder cycloadditions was used to protect and activate specific double bonds in the fullerene cage. In tether-directed method, a special reagent was used, having two groups which can react with fullerene separated by a linking

tether of specific length and geometry. Hence the two groups will react with specific double bonds of the fullerene molecule and later the tether can be removed by cleavage. [19]

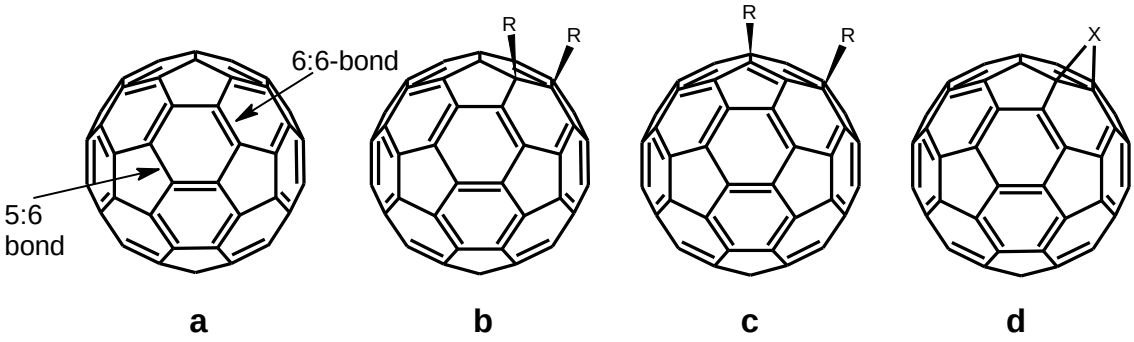


Figure 2.7: Drawings of (a) [5-6] and [6, 6] bonds in C_{60} fullerene (b) 1, 2 addition (c) 1, 4 addition (d) cycloaddition. [18]

In general, Fullerenes are electron deficient and readily undergo electron transfer reaction with electropositive metals, organometallic compounds and nucleophiles. The chemical and physical properties of fullerenes can be modified by the functionalization using chemical reactions. General classifications of chemical reactions that are known to occur for C_{60} are shown in Figure 2.8. Some of the useful reactions for the functionalization of C_{60} are described in the following sections [17]

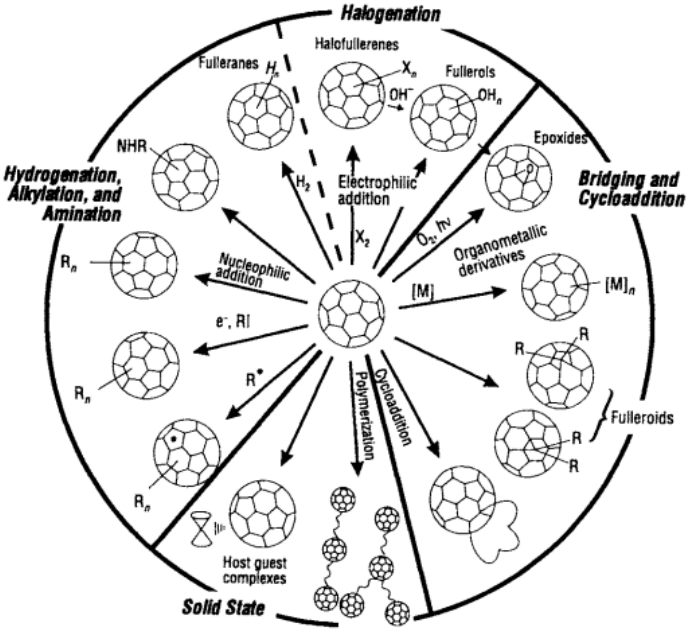


Figure 2.8: Some general categories of reactions known to occur with C_{60}. Here R denotes a functional group [17]

2.5.1 Derivatization by Reduction

Reductions were the first chemical modifications conducted on the fullerene molecule. Fullerene is highly electronegative due to the presence of low energy triply degenerate lowest unoccupied molecular orbitals namely LUMO (t_{1u}-symmetry) and LUMO+1(t_{1g}-symmetry). Therefore C_{60} can accept up to six electrons. [11]

Nature of the solvent, electrolyte and temperature can influence the reduction potential of fullerene. Particularly the donor-acceptor properties, Lewis basicity and hydrogen-bonding interaction of the solvent have notable influence. The dependence of reduction potential of fullerene on solvents is shown in Table 2.1 [11]

Table 2.1: Reduction potentials [mV vs $Me_{10}Fc/Me_{10}Fc+$] of C_{60} in different solvents. [11]

Solvent	**$C_{60}^{0/1-}$**	**$C_{60}^{1-/2-}$**	**$C_{60}^{2-/3-}$**	**$C_{60}^{3-/4-}$**
Acetonitrile		-735	-1225	-1685
DMF	-312	-772	-1362	-1902
Pyridine	-343	-763	-1283	-1813
Aniline	-396	-693	-1158	-1626
Benzonitrile	-397	-817	-1297	-1807
Nitrobenzene	-406			
Benzyl alcohol	-443	-817		
Dichloromethane	-468	-858	-1308	-1758
THF	-473	-1063	-1633	-2133
ODCB	-535	-907	-1360	-1841
Chloroform	-554	-908		

Reduction reactions of fullerenes are found to be one-electron transfer processes. The suitable solvent for the electrochemical reduction of C_{60} was a mixture of acetonitrile and toluene, with reduction potentials appearing in an interval of 450±50 mV. The reduction potentials required for the stepwise formation of hexa-anion are shown in Table 2.2 [11]

Table 2.2: Reduction potentials of C_{60}. [11]

Solvent	**$C_{60}^{0/1-}$**	**$C_{60}^{1-/2-}$**	**$C_{60}^{2-/3-}$**	**$C_{60}^{3-/4-}$**	**$C_{60}^{4-/5-}$**	**$C_{60}^{5-/6-}$**
PhMe/MeCN (mV vs FC/FC^{+})	-980	-1370	-1870	-2350	-2850	-3260

Apart from the electrochemical method the reduction of fullerenes can be accomplished either by reduction with metals or by reduction with organic donor molecules. Electropositive metals such as alkali and alkaline earth metals can

chemically reduce fullerene to fulleride anions in solution. Titration of suspension of C_{60} in liquid ammonia against a solution of Rb in liquid ammonia results in the generation of anions C_{60}^{n-} (n=1-5). Using THF as solvent, fulleride anions can be generated by reduction of fullerenes using Li metal under sonication. However in order to achieve specific stoichiometry of the alkali fullerides generated, reduction was always carried out in the presence of crown ethers or using electron carriers such as corranulene or naphthalene. [11]

Alkali metal doped fullerides M_nC_{60} (M= Na, K, Rb, Cs) and mixed alkali doped fullerides $M^1{}_nM^2{}_m$ (M^1, M^2= Li, Na, K, Rb, Cs) were synthesized by reacting stoichiometric amounts of metal and C_{60} at 200˚C in a sealed tube. Compounds with stoichiometry M_nC_{60} (M= Na, n=2, 3; M=K, n=3) were synthesized by reacting solid C_{60} with solid MH or MBH_4. As compared with alkali metals, handling of MH and MBH4 were convenient.[11, 20] Fullerides Li_nC_{60} (n= 0.5, 2,3,4 & 12) were prepared by solid state electrochemical doping using metallic lithium as negative electrode and polyethylene oxide lithium perchlorate($P(EO)_8LiClO_4$) polymer film as electrolyte. [21]

Alkali metal fullerides exhibits the same fcc (face centered cubic) structure of parent C_{60} fullerene or may exist as a bcc (body centered cubic) and bct (body centered tetragonal) structures. Schematic representation of C_{60} and M_nC_{60} structures are shown in Figure 2.9 [17]

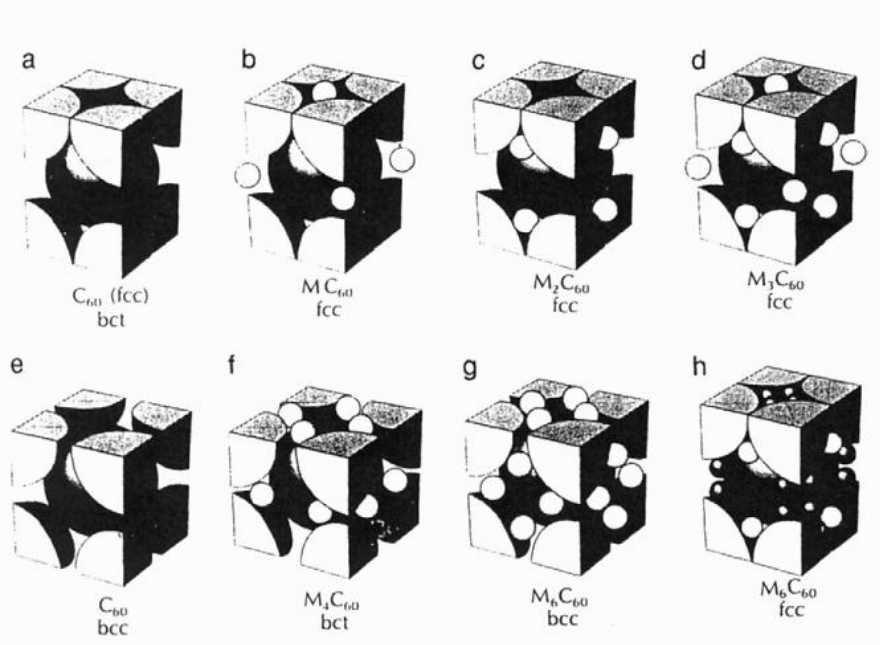


Figure 2.9: Schematic representation of C_{60} and M_nC_{60} [17]

Reductions of C_{60} with alkaline earth metals and with less electropositive metal such as mercury were also reported. Heating a mixture of alkaline earth metal and C_{60} under inert atmosphere in a sealed tube at 550-800˚C yield corresponding alkaline earth metal fullerides such as Ca_5C_{60}, $Ba6C_{60}$, Ba_xC_{60}(x= 3-6) or Ba_4C_{60} and Sr_4C_{60}. [20]

Reduction of C_{60} using mercury can be achieved in the presence of tetra hexylammonium bromide (THA)Br in THF. [11]

Organic or metal organic donor molecules can also be used for the reduction of C_{60}. Charge-transfer (CT) complexes such as tetrakis (dimethylamino) ethylene (TDAE) can be used as electron donor to synthesize [TDAE] $^{+}C_{60}^{-}$ which exhibit ferromagnetic property with Curie temperature of 16.1K. [11] Other donors used for the reduction of C_{60} to anion were Cobaltocene ($CoCp_2$) [22], Fe^{I} (C_5H_5) (C_6Me_6) and decamethylnickelocene Ni $(C_5Me_5)_2$ [23] as shown in Figure 2.10

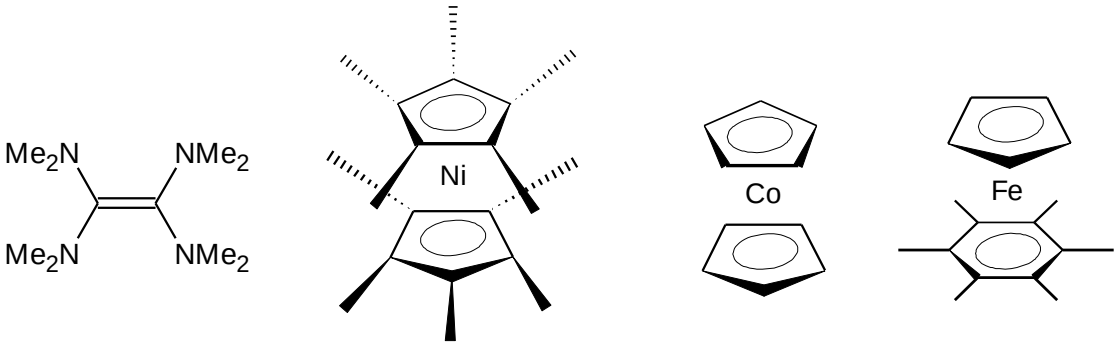


Figure 2.10: Organic donors used for the reduction of C_{60} [11]

2.5.2 Nucleophilic Additions

Nucleophiles such as carbon, nitrogen, phosphorous and oxygen undergo reaction with C_{60} to form intermediate $Nu_nC_{60}^{n-}$ which readily reacts with electrophiles to form stable compounds. Thus, electrophiles such as H^+ or carbocations give $C_{60}E_nNu_n$, neutral electrophiles EX give $C_{60}E_nNu_nS_Ni$ reaction yielded methanofullerenes and cyclohexanofullerenes and oxidation gave $C_{60}Nu_2$.[11] As mentioned earlier, 1, 2 additions was the most favored, even though 1, 4 and 1, 6 additions also happen depending on steric demands. [25]

Addition of organolithium and Grignard reagents of alkyl, phenyl and alkynyl groups and sodium cyanide was used for the functionalization of C_{60}. The intermediate $R_nC_{60}^{n-}$ can undergo protonation to yield hydrofullerene derivatives ($C_{60}H_nR_n$) or can react with MeI to form $C_{60}Me_nR_n$. The scheme for the nucleophile addition is shown in Figure 2.1. The purification of 1, 2 organodihydrofullerenes was carried out either by preparative HPLC or flash chromatography using mixture of toluene and hexane as eluent. In order to achieve the maximum yield, 1.2 equivalents of organolithium compounds or 5-27 fold excess of Grignard reagent were used. [11] Successful isolation of intermediate $t\text{BuC}_{60}^{-}\text{Li}^{+}\cdot 4\text{CH}_3\text{CN}$ was carried out by reacting stoichiometric amount of 1.2M *tert*-butyl lithium with C_{60} in benzene and subsequent recrystallization in acetonitrile. [24]

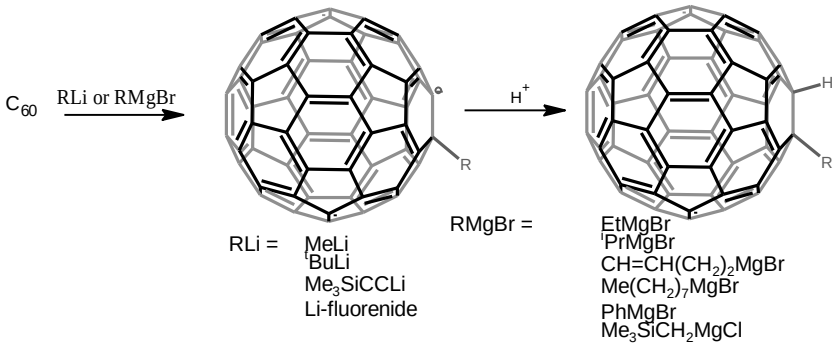


Figure 2.11 Scheme for hydroalkylation for fullerene. [10]

Earliest alkynyl derivatives of C_{60} were (trimethylsilyl)ethynyl and phenylethynyl-dihydro[60] fullerene synthesized from [(trimethylsilyl)ethynyl]lithium and [phenylethynyl]lithium respectively by the reaction with C_{60} in toluene and subsequent protonation.[26] Reactions with different Li acetylides Li-C≡C–R with R= hexyl and benzyl ether dendrons and various electrophiles such as alkyl, benzyl, cycloheptatrienyl-, benzoyl-, vinylether-, formaldehyde and dichloroacetylene to quench the intermediate Li-fulleride were also reported. [11] The scheme for the synthesis of alkynyl derivatives of C_{60} using acid, benzyl bromide and formaldehyde is shown in Figure 2.12

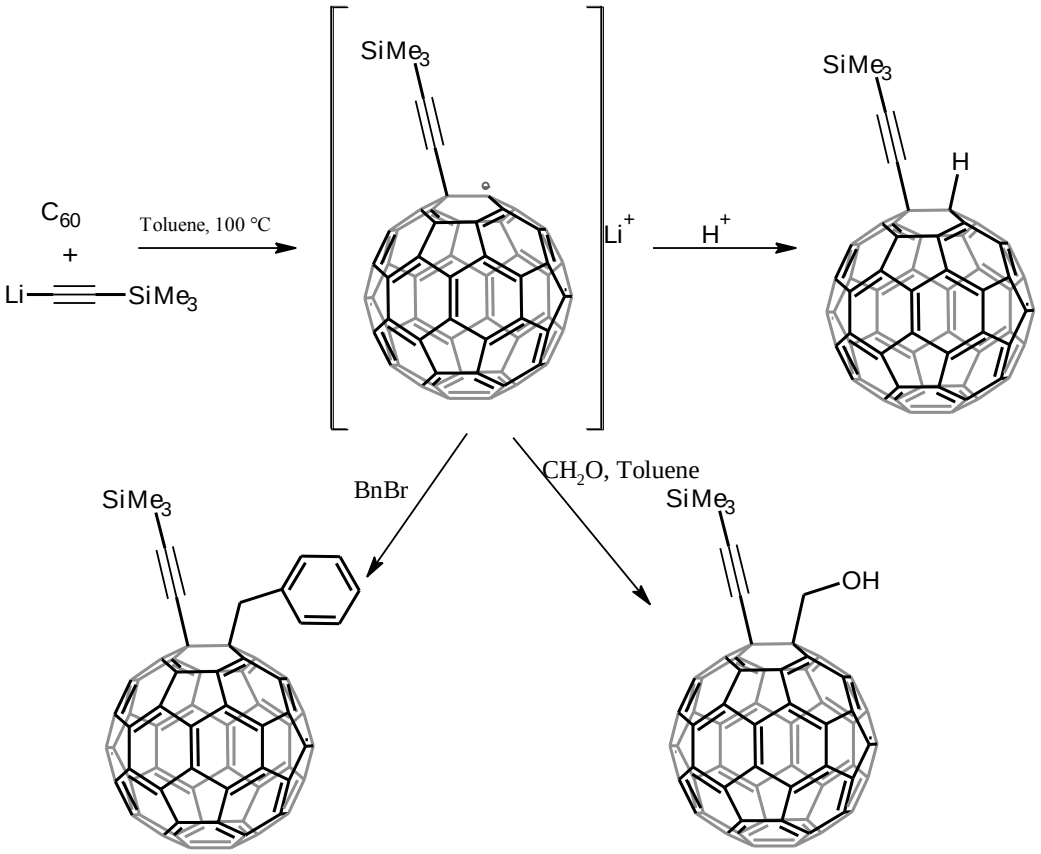


Figure 2.12: Scheme for preparation of alkynyl derivatives of C_{60} using acid, benzyl bromide and formaldehyde [11]

As mentioned earlier, the intermediate anion RC_{60}^- generated by nucleophilic addition can also be stabilized by intramolecular SNi mechanism, provided R should contain a leaving group. Bingel demonstrated the synthesis of cyclopropane derivative of C_{60}, generating carbon nucleophile by deprotonation of α-halo esters or α- halo ketones. Bingel reaction for cyclopropanation of C_{60} with diethyl bromomalonate in toluene with NaH as auxiliary base is shown in Figure 2.13 [11]

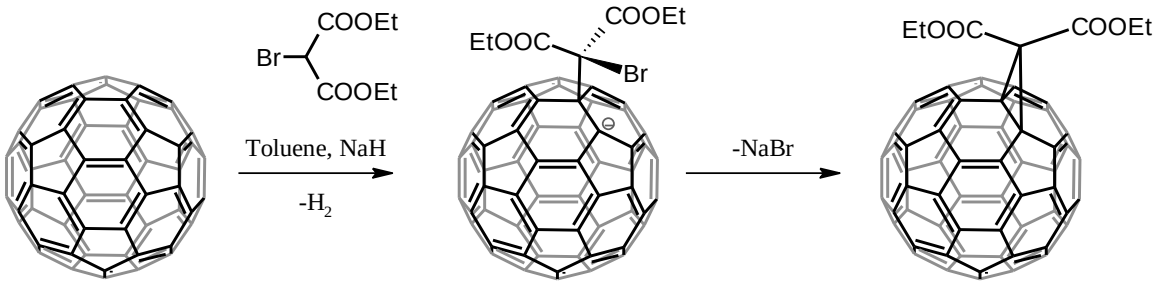


Figure 2.13: Bingel reaction for cyclopropanation of C_{60} [11]

Later 1,8-diazobicylo[5.4.0]undec-7-ene (DBU) was used as auxiliary base for the cyclopropanation of C_{60} with methyl-2-chloroacetylene, ω-bromoacetophenone and densyl chloride.[27] The yields of the reaction can be improved by the *in situ* generation of α-halo esters or α- halo ketones from the reaction of malonic derivatives or 1,3- diketones with iodine or tetrabromomethane and a base. [28] Solvent free Bingel reaction using diethylbromomalonate and inorganic base Na_2CO_3 under the mechanochemical 'high-speed vibration milling' conditions was reported with high yield (40-50%).[29] Apart from Bingel reaction, phosphorous and sulphur-ylides [30], fluorine-ion-mediated reaction with silylated nucleophiles were used to synthesize 1, 2-methano-[60] fullerenes.[31] In addition to that, synthesis of methanofullerene with a formyl group at bridgehead-carbon ie on the methano carbon was also demonstrated by via sulphur-ylide. [32]

Bis(alkoxycarbonyl)methano addends formed by the Bingel reaction can be removed either by electrochemical reduction [33] or by chemical reaction with amalgamated Mg or Zn/Cu-couple.[34] Furthermore, bis(alkoxycarbonyl)methano addends can be removed in the presence of pyrrolidine-addends. The methaniminomethano bridge was found to be stable under these conditions (Figure 2.14). Thus for the synthesis of fullerene multi-adducts, Bingel addends can be used as protecting and reversible directing group. [34].

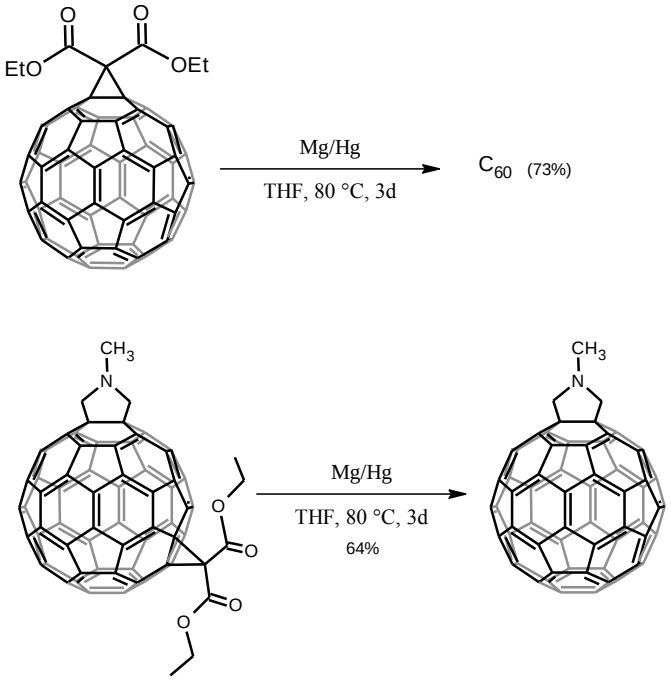


Figure 2.14: Retro Bingel with and without bis adducts [34]

Electron withdrawing substituent such as cyanide can be attached to fullerene by the reaction of LiCN or NaCN with C_{60}. The introduction of cyanide group compensates the decrease in electron affinity caused by the loss of double bond due to the addition of alkyl nucleophiles. The intermediate anion formed during the process can react with various electrophiles to generate different products as shown in Figure 2.15 [35]

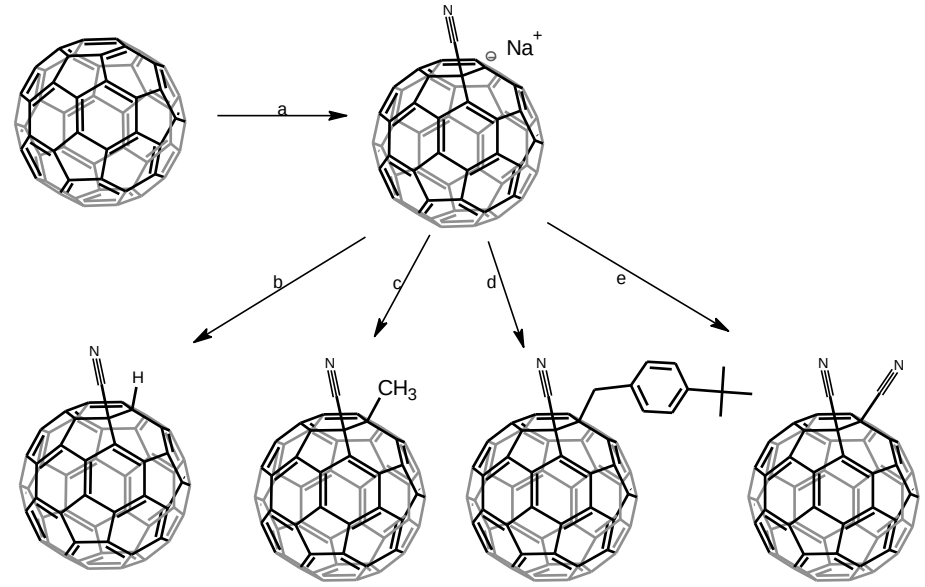


Figure 2.15: Reagents and conditions: (a) NaCN, ODCB/DMF, rt; (b) trifluoroacetic acid, rt, 29%; (c) methyl trifluoromethanesulfonate, rt, 10%; (d) 4-tert-butyl- benzyl bromide, 70˚C, 11%; (e) p-toluenesulfonyl cyanide, rt, 61 % [35]

Fullerenes undergo nucleophilic addition with primary and secondary aliphatic amines. The reaction proceeds through the formation of C_{60} radical anion resulting from the single electron transfer from the amine to C_{60} and subsequent radical recombination. The resultant zwitterions can either undergo proton transfer from amine or oxidation and subsequent deprotonation and radical recombination as shown in Figure 2.16 [11]

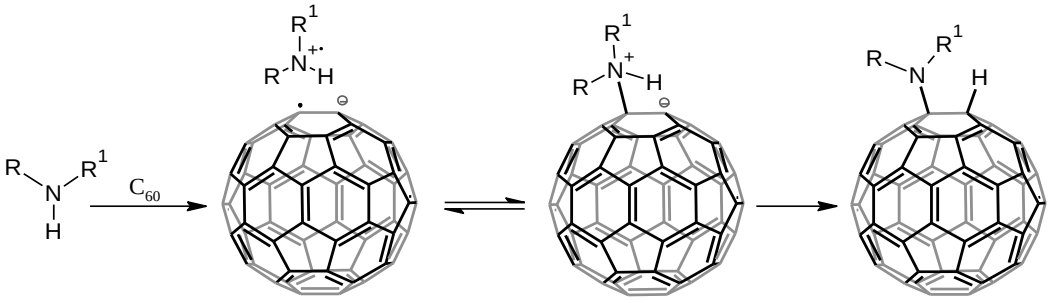


Figure 2.16: Mechanism for addition of primary and secondary amine to C_{60} [11]

Since the reaction proceed through a radical mechanism, complex mixture of amino adducts was formed. Formation of hydroamination products occur only under inert atmosphere. [11] Monoazacrown ether adduct of fullerenes were synthesized (shown in Figure 2.17). The Langmuir and Langmuir-Blodgett (LB) films prepared using adduct were found to exhibit second-order nonlinear susceptibilities. [36]

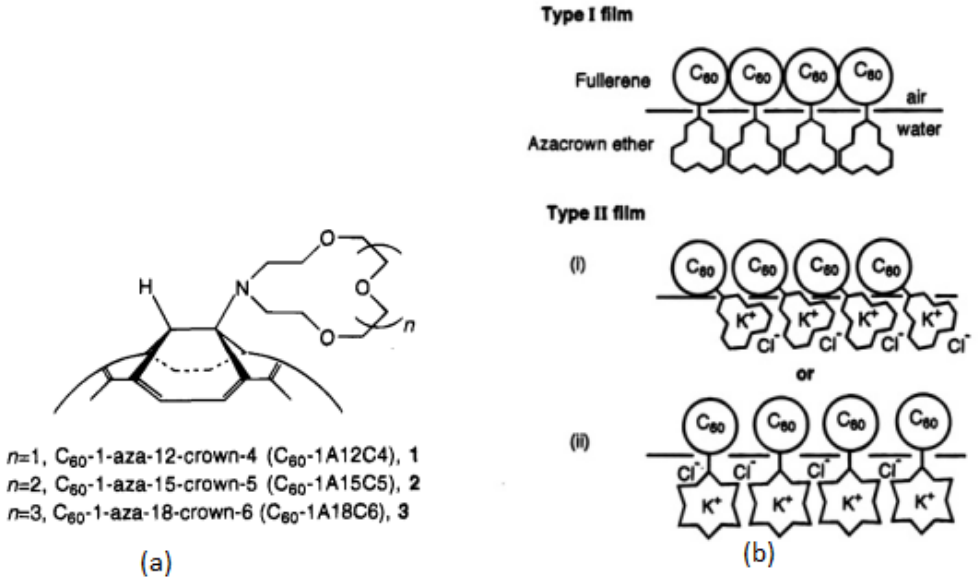


Figure 2.17: (a) Fullerene-aza-crown ethers (b) Schematic representation of different morphologies of their Langmuir films [36]

Unlike primary and secondary amines, tertiary amines form neutral and stable charge transfer (CT) complex. Depending on the nature of the tertiary amine, the initially formed CT complex can undergo cycloaddition, or insertion of C_{60} into an alkyl-CH bond happens. [11]

The reaction of amines with C60 can also be utilized for the formation of monolayers. C_{60} can be covalently attached to self-assembled monolayers (SAMs) as shown in Figure 2.18. [37]

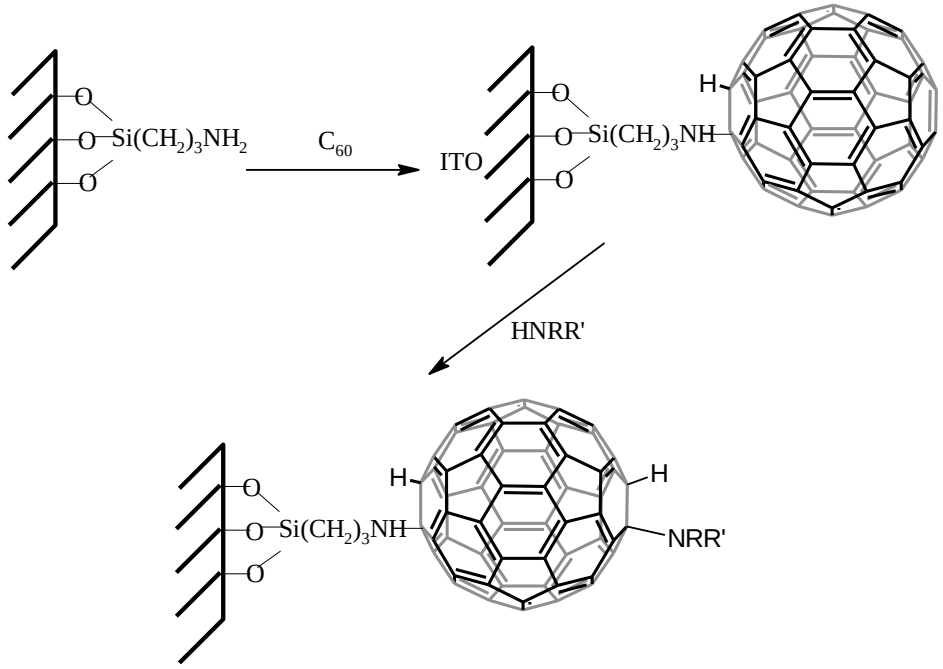


Figure 2.18: Synthetic scheme for the modification of oxide surfaces with C_{60} [37]

Phosphorous nucleophiles can undergo nucleophilic addition with C_{60}. Even though phosphine was inert to nucleophilic addition, it can be attached indirectly. More nucleophilic reagent such as lithiated phosphines and phosphites were found to be useful for addition. Moreover, the presence of phosphorous-borane bond in phosphine-borane complex helps the reaction by stabilizing the phosphorous atom against oxidation, and also simplifies the product separation. Later the BH_3 group can be removed by treatment with diazabicyclo [2.2.2]octane (DABCO) as shown in the synthesis of P-chiral phosphine- C_{60} adduct shown in Figure 2.19 [38]

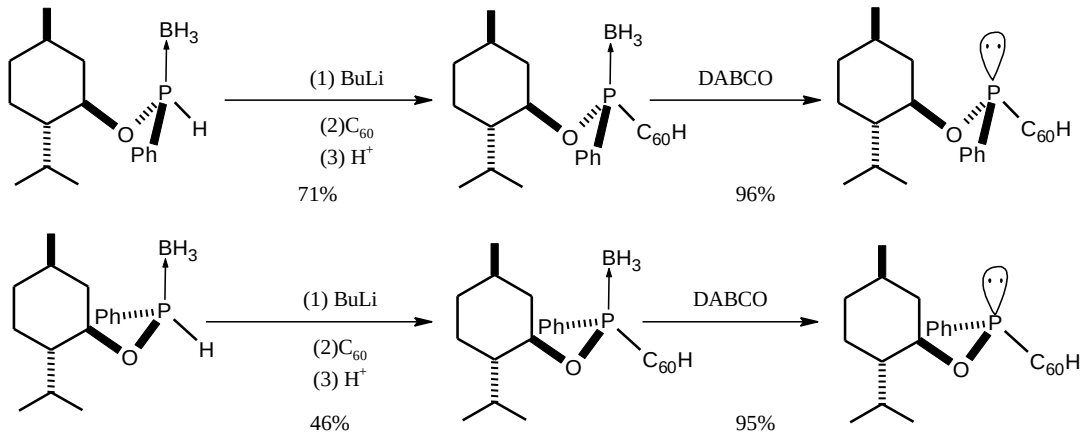
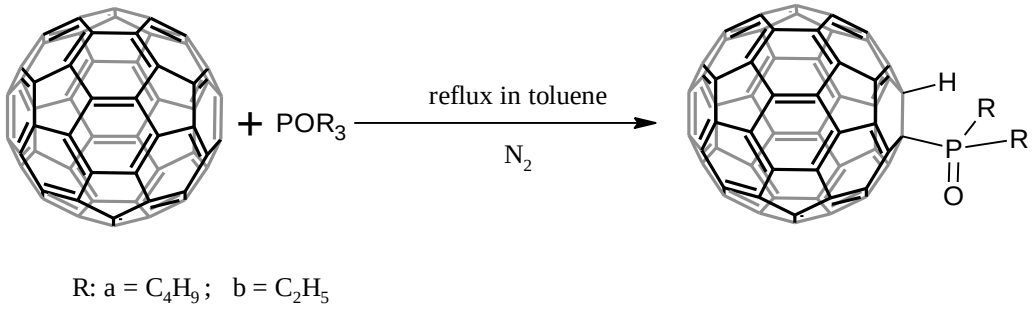


Figure 2.19: Scheme for the synthesis of P-Chiral phosphine-C_{60} adduct

Phosphine oxide can also undergo nucleophilic addition to C_{60} under reflux in toluene (Figure 2.20). [39]



R: a = C_4H_9 ; b = C_2H_5

Figure 2.20: Scheme for nucleophilic addition of phosphine oxide to C_{60} [39]

2.5.3 Cycloaddition

The dienophilic character of [6, 6] double bonds of C_{60} makes it suitable for cycloaddition. Diels-Alder reaction ([4+2]-cycloaddition) occurs with unactivated dienes such as 2,3-dimethyl butadiene and monoterpene myrcene to form 1,2[2',Y-dimethyl-2'-butene-l',4'-diyl]-l,2-dihydro-[60]fullerene and 1,2[2'-(4''-methyl-Y'-pentenyl)-2'-butene-l',4'-diyl]-l,2-dihydro-[60]fullerene, which indicates the high reactivity of C_{60}. [40]

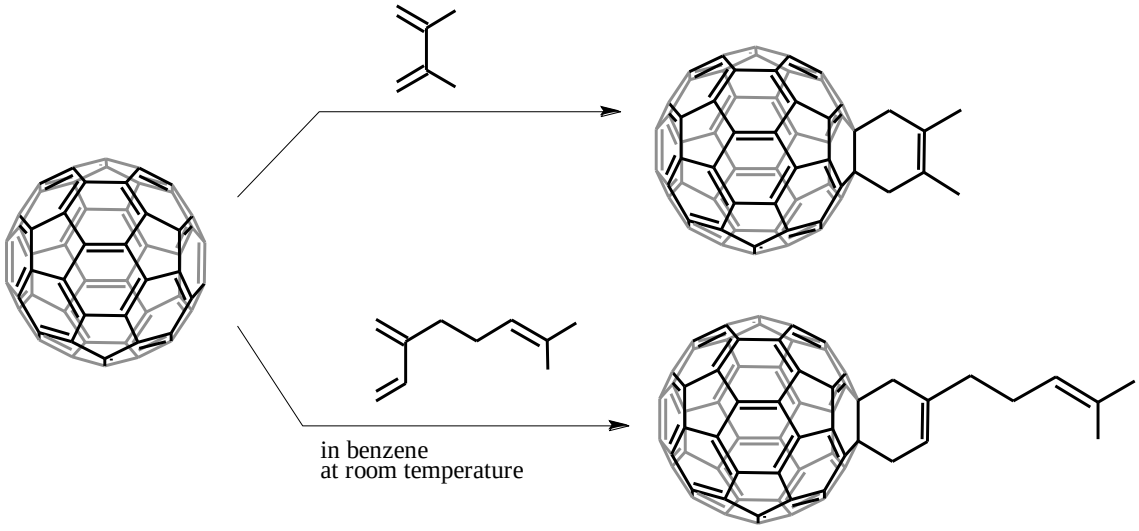


Figure 2.21: Scheme for the synthesis of cycloaddition products of C_{60} [40]

Diels-Alder products of C_{60} with acenes such as anthracenes, tetracenes and pentacenes were also reported. However the thermal stability of C_{60}-anthracene monoadduct was not high. The anthracene moiety is readily cleaved at higher temperatures yielding C_{60} in retro Diels-Alder reaction. (Figure 2.22) [41]

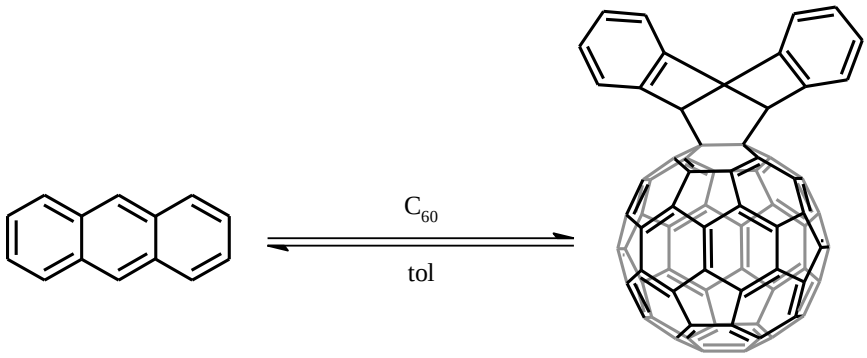


Figure 2.22: Scheme for reversible Diels-Alder reaction between C_{60} and anthracene. [41]

Reactivity of larger acenes such as tetracene and pentacene were high when compared with anthracene and th products were less prone to decomposion. Large acenes that can add more than one C_{60} fullerene were also reported. With suitable directing substitutents such as phenyl, a syn–diastereoselective mode of C_{60} fullerene additions forms due to favorable π-π stacking interaction of the adjacent fullerene moieties. Synthesis of cis,cis-tris[60]fullerene-tetraphenylheptacene adduct from 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene and C_{60} proceeds in this way (Figure 2.23). [41]

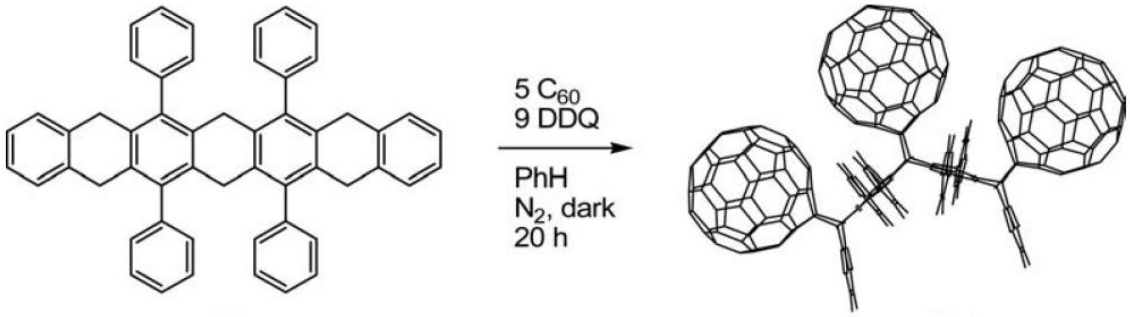


Figure 2.23: Synthesis of cis, cis-tris [60] fullerene-tetraphenylheptacene adduct. [41]

In situ generation of o-quinomethane intermediate was another useful way for synthesizing stable Diels-Alder adducts of C_{60}. 4-Carboxy-o-quinodimethane was prepared *in situ* by bromine elimination from 3,4-bis(bromomethyl)-benzoic acid with the base (KI), in boiling toluene using 18-crown-6 as phase transfer catalyst. Quinodimethane thus formed reacts with C_{60} to form stable Diels-Alder adduct as

shown in Figure 2.24.[42]

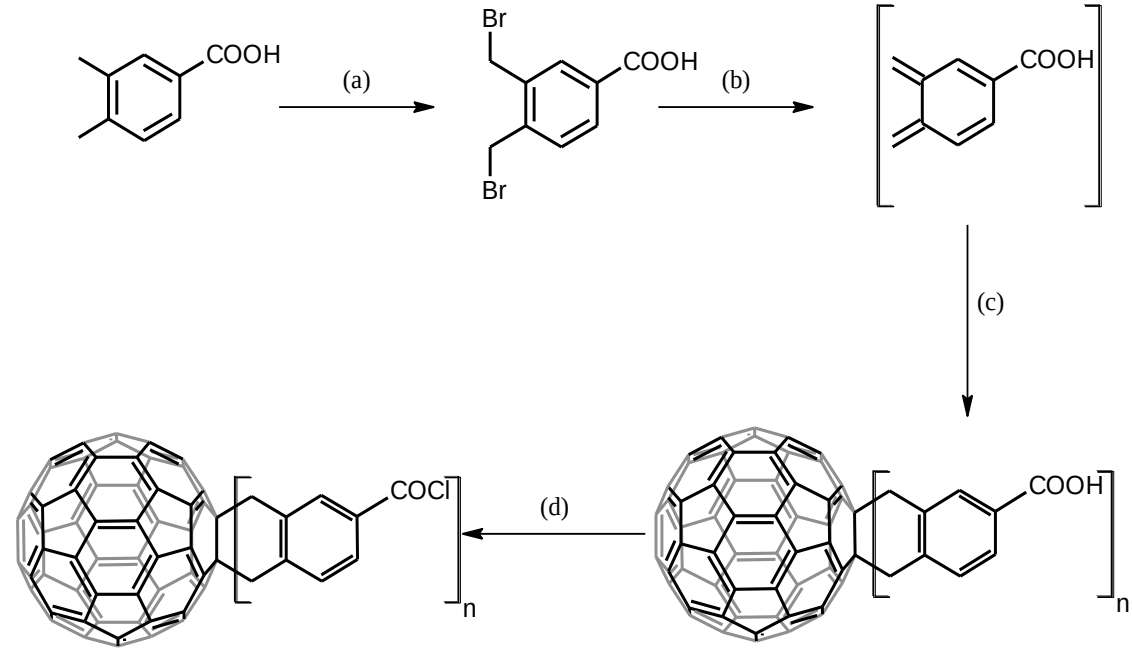


Figure 2.24: Synthesis of the carboxylic C_{60} adducts: (a) CCl4; NBS (2.4 equiv); dibenzoyl peroxide (0.1 equiv); (b) toluene; KI (4 equiv); 18-crown-6 (3 equiv); (c) $SOCl_2$. [42]

Hetero Diels-Alder adducts of C_{60} with hetero atoms such as sulphur [43] and nitrogen [44] were also demonstrated. Thiochroman-fused C_{60} derivative was synthezied by the *in situ* generation of o-thioquinone methide by the thermal electrocyclic ring opening of benzothier and subsequent reaction with C_{60} in o-dichlorobenzene (Figure 2.25). [43]

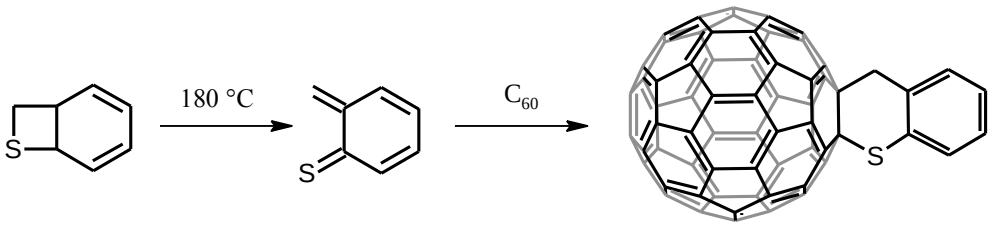


Figure 2.25: Synthesis of thiochroman-fused fullerene adduct [43]

Due to the 1,3-dipolarophile character of the C_{60}, fullerene undergo [3+2] cycloaddition with diazomethanes, diazoacetates, diazoamides, diazomethylphosphonate and diazoketones to form a variety of methano-bridged adducts. [11] The subsequent expulsion of N_2 by thermal or photochemical reaction of the cycloadduct formed by the diazomethane addition of C_{60} yield methano-bridged fullerenes with [5, 6] ring opened fulleroid as major product, and [6,6] ring closed methanofullerene as minor product. [45] Synthesis of phenyl-bridged fullerene dimer from phenylene-bis(diazomethane) was steered by this mechanism (Figure 2.26) [46]

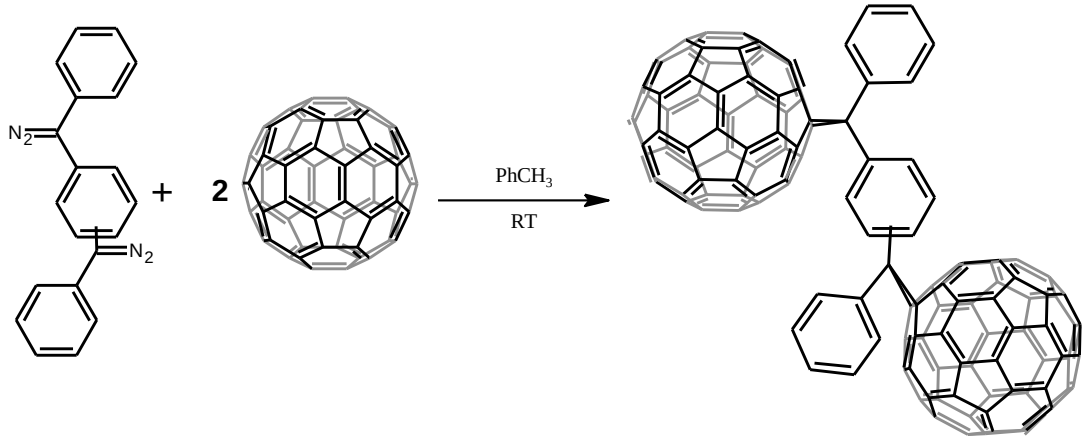


Figure 2.26: [3+2] cycloaddition of phenylene-bis (diazomethane) to form phenyl-bridged fullerene dimer [46]

One-pot procedure with *in situ* generation of diazocompounds from tosylhydrazone anion at 70˚C by the base-induced (sodium methoxide or butyllithium) decomposition of tosylhydrazones was also developed. [47]

Azomethine ylides can undergo [3+2] cycloaddition with the [6, 6] bond of C_{60} to give fulleropyrrolidines in a reaction known as "Prato reaction". Reaction is highly selective towards [6, 6] bond of C_{60} and is widely used for the functionalization of fullerenes. [11] Azomethine ylides can be generated *in situ* by the decarboxylation of immonium salts derived from condensation of α-aminoacids with aldehydes or ketones. N-methyl pyrrolidine derivative of C_{60} was synthesized by using the above mentioned mechanism (Figure 2.27) [48]

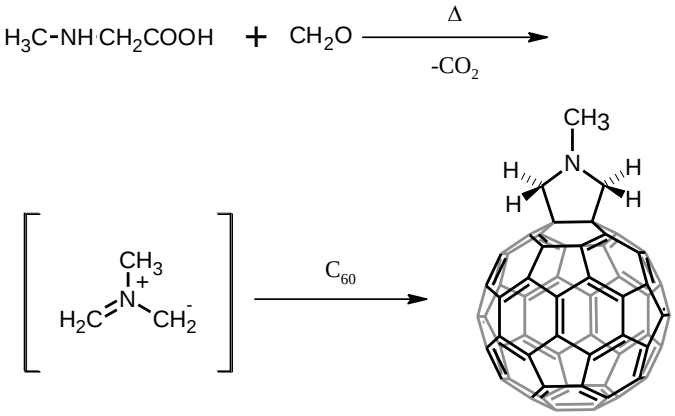


Figure 2.27: synthesis of N-methyl pyrrolidine fullerene by Prato reaction. [48]

Another method for the *in situ* generation of azomethine ylides is the thermal ring opening of aziridine or related compounds in toluene. (Figure 2.28) [48]

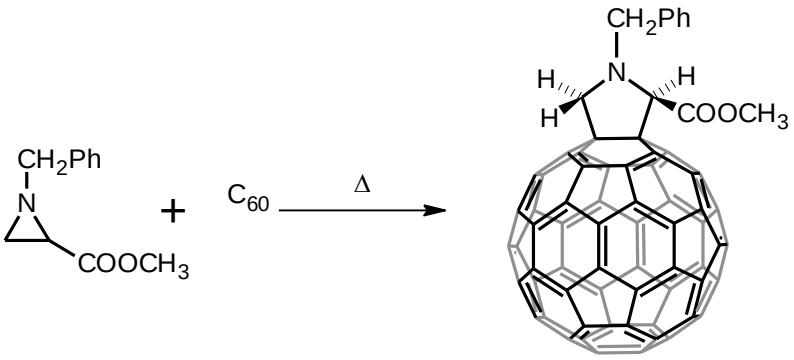


Figure 2.28: Prato reaction using *in situ* generated azomethine ylide by thermal ring opening of aziridine. [48]

Donor-acceptor dyads or triads of C_{60} and porphyrins [49], tetrathiafulvalenes (TTFs), ferrocenes etc. [50] with suitable aldehyde or ketone functionality, can be synthesized by Prato reaction. (Figure 2.29)

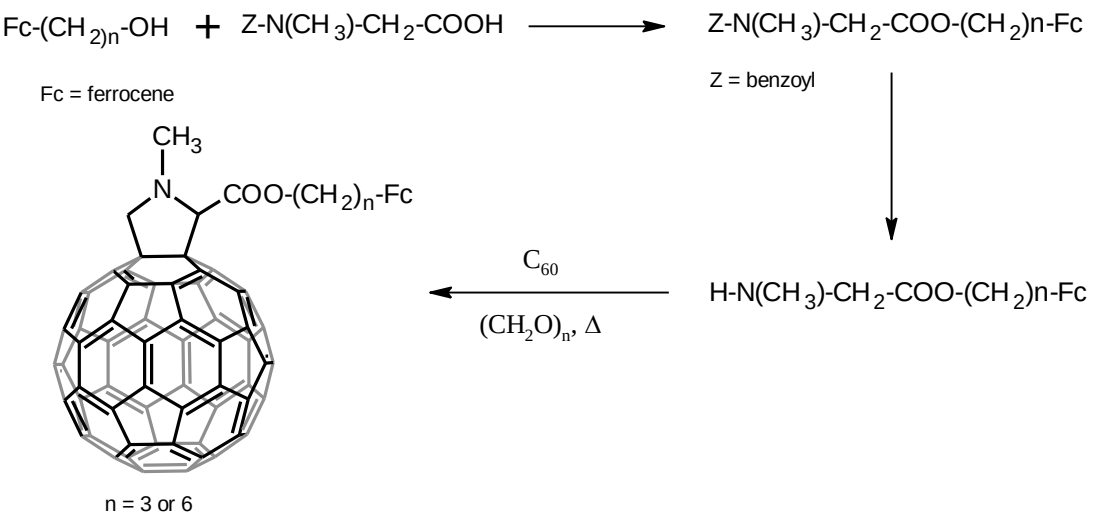


Figure 2.29: Synthesis of Ferrocene-fullerene dyad by Prato reaction [50]

The [2+2] cycloaddition between C_{60} fullerene and benzyne were also reported. Benzyne species were generated *in situ* by the reaction of anthranilic acid derivative and isoamyl nitrite in toluene or by oxidation of 1-aminobenzotriazole with lead tetraacetate. [51]

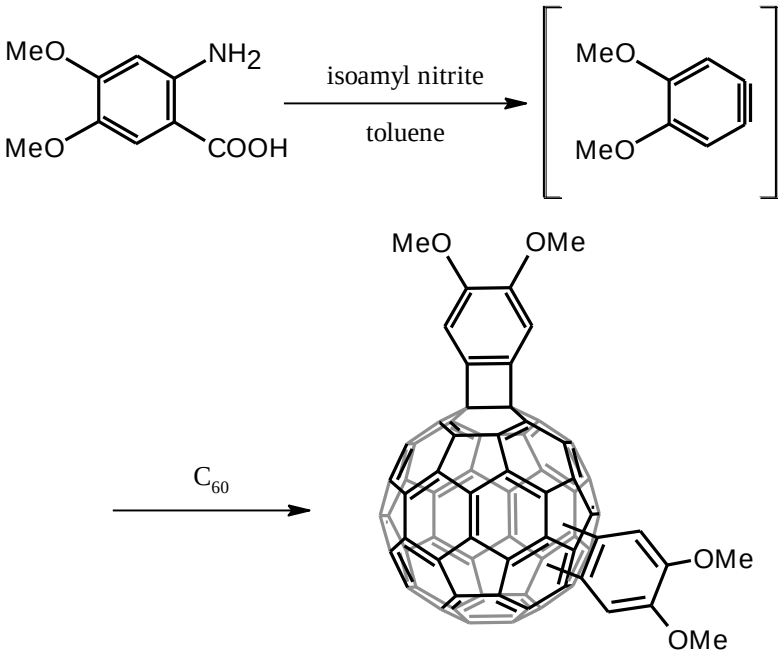


Figure 2.30: [2+2] cycloaddition between C_{60} and benzyne. [51]

Similarly enones can also react with [6, 6] bond of C_{60} by photochemical [2+2] cycloaddition as shown in Figure 2.31. [52]

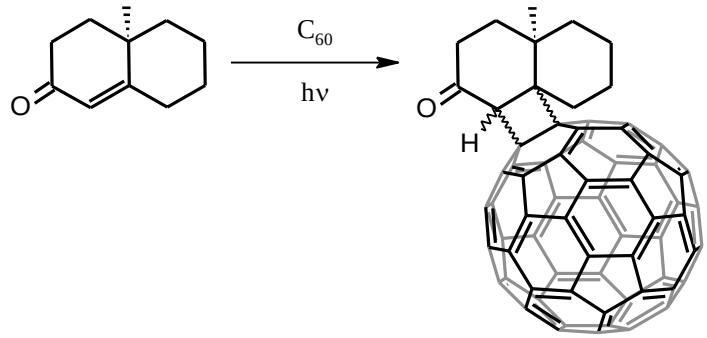


Figure 2.31: [2+2] cycloaddition between C_{60} and enone. [52]

Generally, carbenes undergo [2+1] cycloaddition to the C_{60} to yield 1, 2-methano-bridged monoadducts. Carbene was generated by the thermal extrusion of N_2 from O-benzyl and O-pivaloyl-protected diazirine as described in Figure 3.32 [11]

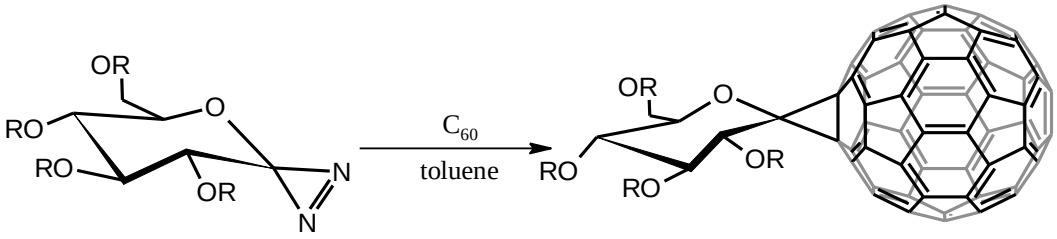


Figure 2.32: Addition of [2+1] cycloaddition of carbine to C_{60}. [11]

2.6 Methods for immobilization of fullerene on surfaces.

Surface modification using fullerenes is of great research interest due unique physical and chemical properties of these compounds. For practical applications, pristine fullerenes are rather useless mainly owing to the poor solubility. However this weakness can be overcome by suitable modification of C_{60}. The surface coating with fullerenes may create a new class of hybrid materials having potential applications in various fields. The deposition conditions or disorder in surface structure may affect the physical properties of fullerene-containing films adversely. Therefore robust methodologies are highly essential for the successful incorporation of fullerenes onto the solid surfaces. The important techniques for immobilization of fullerenes on solid surfaces are either by self-assembly monolayer (SAM) methodology or by preparing monolayers or thin films by Langmuir and Langmuir-Blodgett (LB) deposition technique. [53]

2.6.1 Strategies for self-assembled monolayers of C_{60}

One strategy for the self-assembling of C_{60} monolayers on solid surface was to functionalize the fullerene with suitable anchors that can react with the surface. The anchors may include thiol, phosphonates, carboxylic acids, siloxanes etc. [53] Preparation of self-assembled monolayer of pyrrolidine-fullerene adducts on Au (111)/ mica substrate was based on strong Au-S interaction. Figure 2.34 [54]

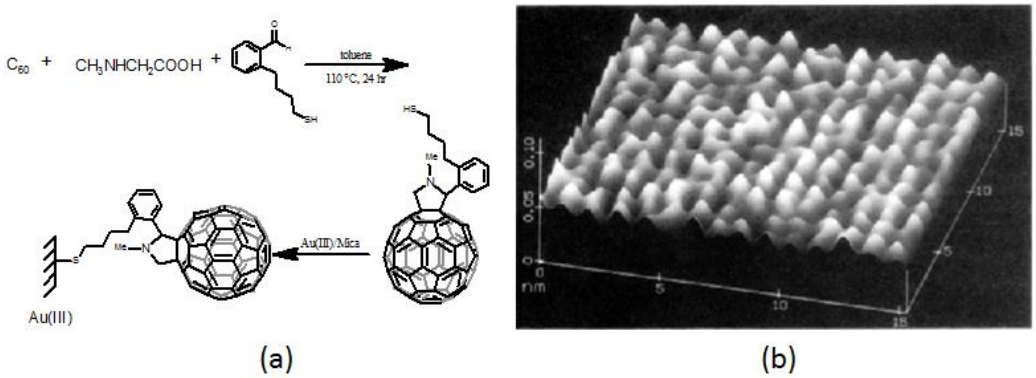


Figure 2.34: Schematic representation of SAMs of pyrrolidine-Fullerene adduct on Au (111)/Mica substrate [54]

Another strategy was to pattern the surface with organic SAMs containing functional groups that can react with pristine C_{60}. Once a monolayer was arranged, addition of C_{60} created an *in situ* bond with the C_{60} and immobilized organic molecule. Immobilization of C_{60} on pyridyl-based monolayer on Au (111) (Figure 2. 35) followed the above mentioned protocol. [55]

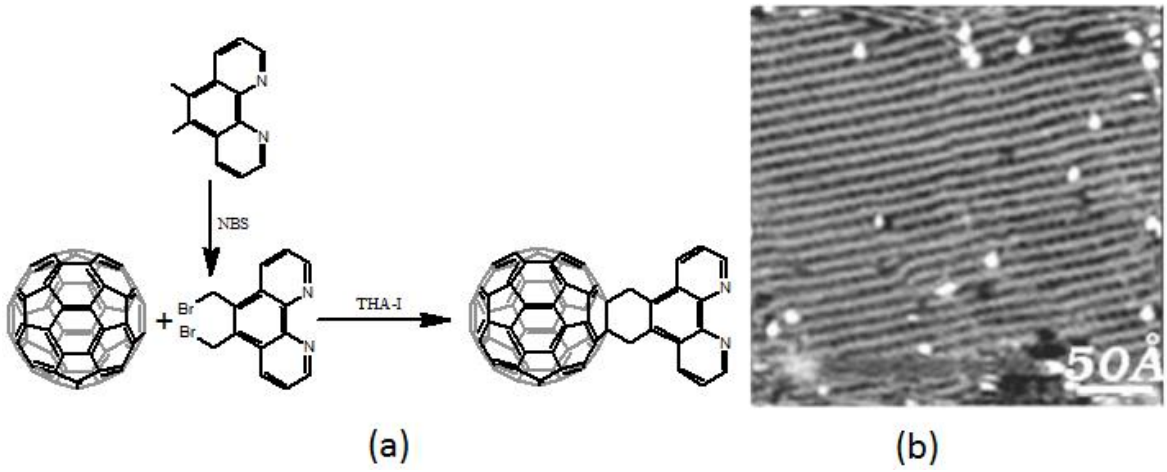


Figure 2.35: (a) Scheme for reaction between phenanthroline and C_{60} (b) STM image showing that the C_{60} derivative molecules intercalate into the phenanthroline chains [55]

Another method for preparing SAMs was to exploit the chemical interactions between fullerene derivatives and monolayer of organic molecules on the surface of solids. The interaction can be either covalent or non-covalent. Surface modification on silica was carried out by a covalent bonding of fullerene derivative having a phenolic group with [4-(chloromethyl) phenyl] silane-terminated silica surface as shown in the Figure 2.36 [56]

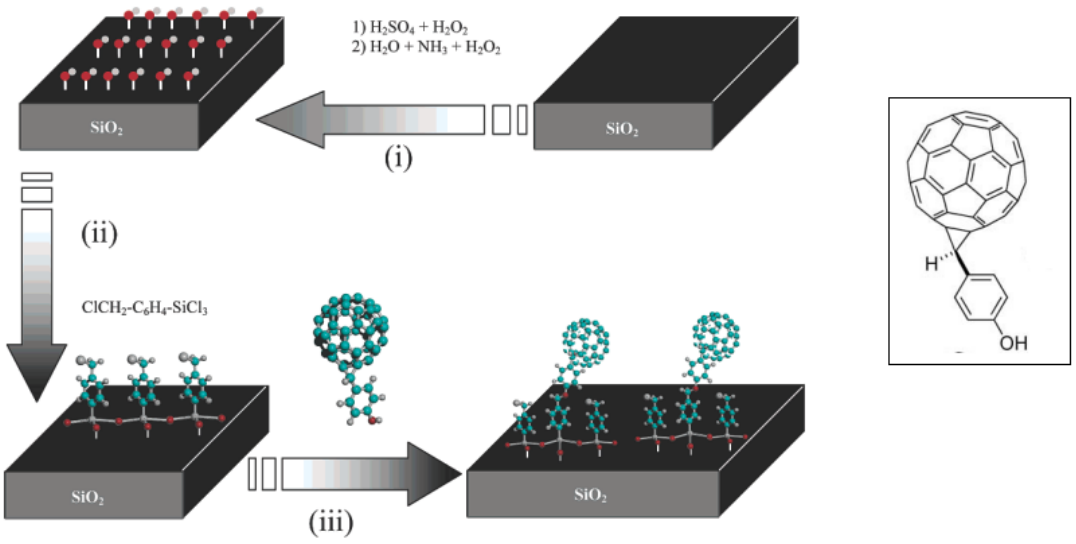


Figure 2.36: Scheme for the synthesis of C_{60} Fullerene Monolayer [56]

The protocol for immobilization of fullerene derivatives by non-covalent interaction was described by Echegoyen and Kaifer for the SAMs of [18]crown-6-derived fullerene on thiolated SAMs terminated in ammonium groups (Figure 2.37) [57]

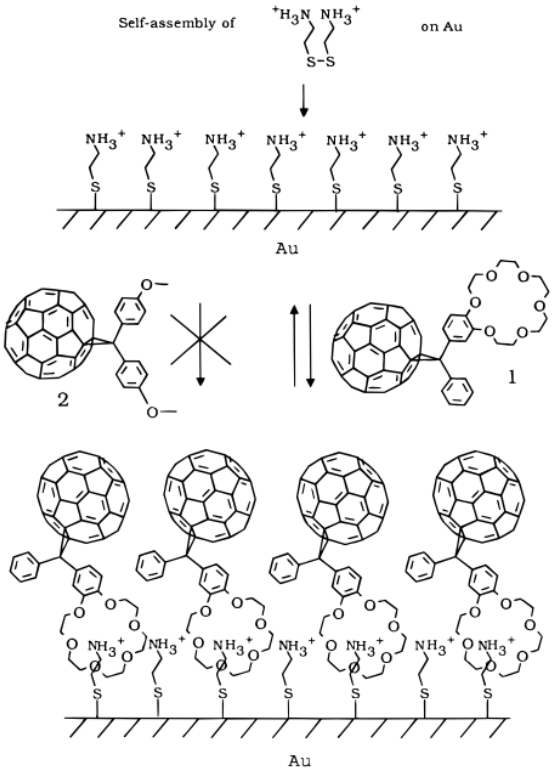


Figure 2.37: Supramolecular assemblies C_{60}-crown ether adduct and SAM of thiolated ammonium salts [57]

Chemical modifications of fullerenes by the attachment of functional groups involve the partial destruction of π-delocalization in the carbon sphere. One way to circumvent the issue was to immobilize the pristine C_{60} on the surface non-covalently. [53] Self-assembly of encapsulated pristine C_{60} spheres between hexacationic homoxacalix [3] arene cage on Au (111) patterned with anionic coating was demonstrated by Shinkai and coworkers. (Figure 2.38) [53, 58, 59]

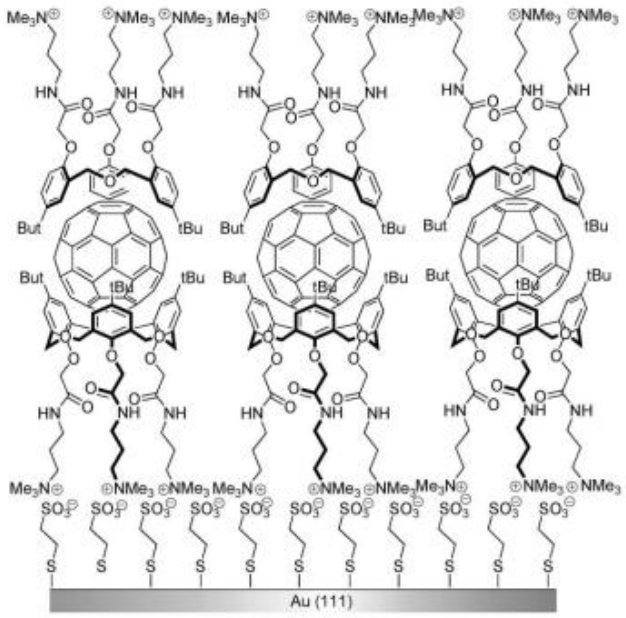


Figure 2.38: SAMs of a hexacationic homooxacalix[3]arene-C_{60} on anionic coated Au(111) surface [53]

2.6.2 Immobilization of fullerene by LB deposition

Formation of LB films of pristine C_{60} was reported by Takayoshi Nakamura *et al* [60]. Langmuir films were formed on pure water using benzene as spreading solvent. The layer was transferred by horizontal lifting method onto a quartz substrate pretreated with hexamethyldisilazane. The AFM image (Figure 2.39a) of the resultant layer on graphite (HOPG) shows the formation of large crystallites and naked graphite surfaces which indicate the incomplete transfer of the film from the water. However in a 1:1 mixture of C_{60} and icosanoic acid, a flat surface was seen by the AFM image, Figure 2.39b. [60]

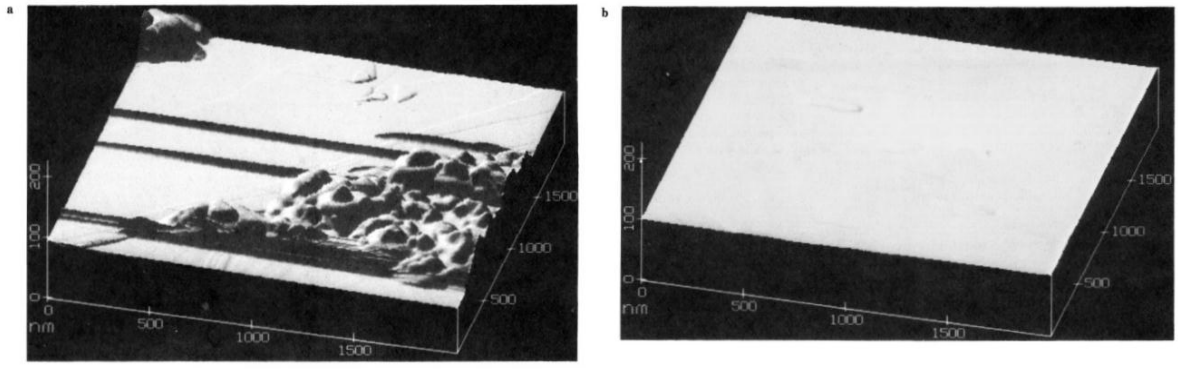


Figure 2.39: AFM image of a one-layered sample on the HOPG substrate: (a) C_{60} and (b) 1:1 mixture of C_{60} and icosanoic acid. [60]

The LB films formed from pristine C_{60} were less stable and their layer-by-layer transfer to solid substrates was not useful for practical purposes. To compensate this, an

alternative method with derivatized fullerenes was developed. Fullerene derivative of bis(triethyeleneglycol monomethyl ether) esters of malonic acid was used for the preparation of high quality stable LB film as shown in Figure 2.40b. [61]

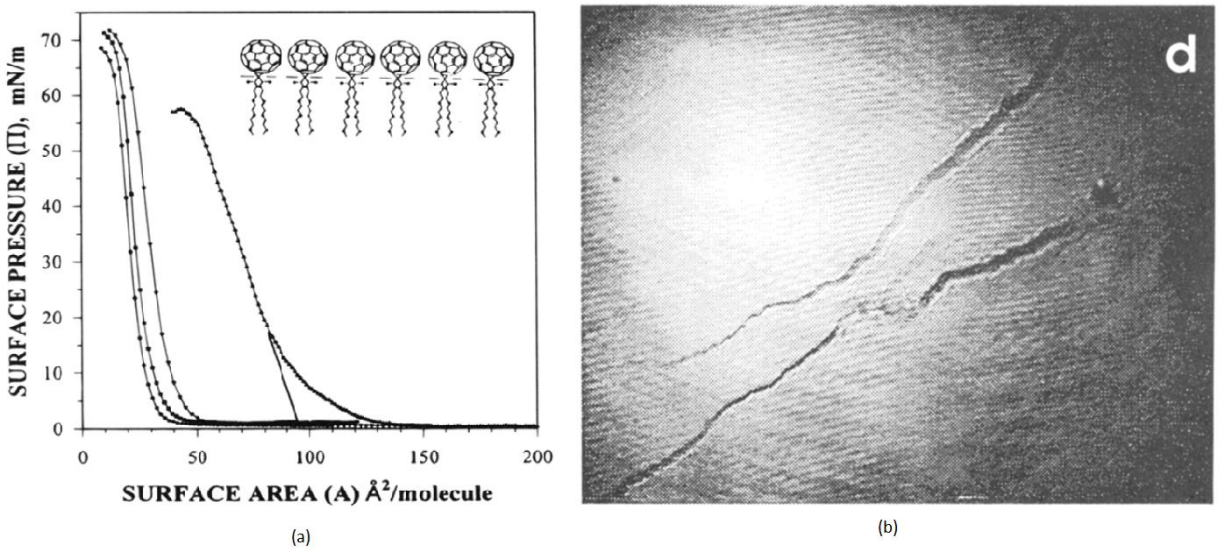


Figure 2.40: (a) Surface pressure (Π) vs surface area (A) isotherms. (▲) indicate the isotherm for Fullerene derivative of bis(triethyeleneglycol monomethyl ether) esters of malonic acid. Insert: Cartoon of a monolayer prepared from 4d showing the immersion of the side chain in water (b) Brewster angle microscopy (BAM) at compression Π =35 mN/m [61]

3 RESULTS AND DISCUSSION

Fullerenes synthesized are grouped according to the anchors attached to the molecules. For the study we have prepared fullerene molecules with different type of anchors such as carboxy, thioacetate and thiol and disulphide moieties. The strategy developed for the synthesis was as follows. The first step of the process was the preparation of linkers derived from malonate. In the second step these linkers were attached to fullerene by the Bingel addition followed by necessary modifications.

3.1 Fullerenes with Carboxy anchors.

Two different compounds were synthesized under this classification. One was a fullerene with a mono carboxy anchor and other with a dicarboxy group. The strategy for the synthesis of these compounds and interpretation of the results are discussed in the following sections.

3.1.1 Synthesis of *tert*-butyl-2-hydroxyacetate

Fullerenes with carboxy anchors were synthesized by multistep approach (Figures 3.1 and 3.4). The scheme for the synthesis of the key intermediate *tert*- butyl-2- hydroxy acetate (3) for the preparation of the linkers is shown in the Figure 3.1 [62]

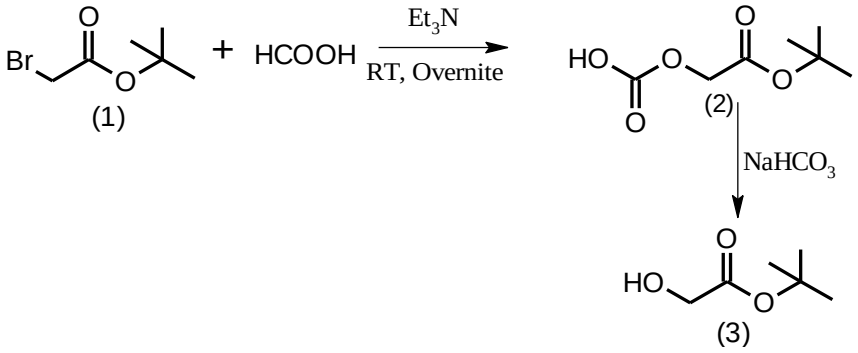


Figure 3.1: Synthesis of *tert* butyl-2- hydroxy acetate

The commercially available *tert*-butyl bromo acetate (1) was used as the starting material for the first step of the synthesis. Formic acid was coupled with compound **(1)** in ethyl acetate in the presence of triethyl amine. Since the addition of triethylamine to formic acid is an exothermic reaction with the generation of white smoke, precaution had taken during the process. The reaction was carried out by stirring the contents at room temperature for 16 hours. Triethylammonium bromide was precipitated out and removed from the reaction mass by filtration and washed with diethyl ether for the complete recovery of the product. The organic layer was washed with saturated brine solution, dried and the solvents were evaporated under reduced pressure to yield *tert*-butyl 2-formyloxyacetate (2). The compound (2) was verified by NMR spectrocsopy. The NMR spectrum of the compound is shown in the Figure 3.2

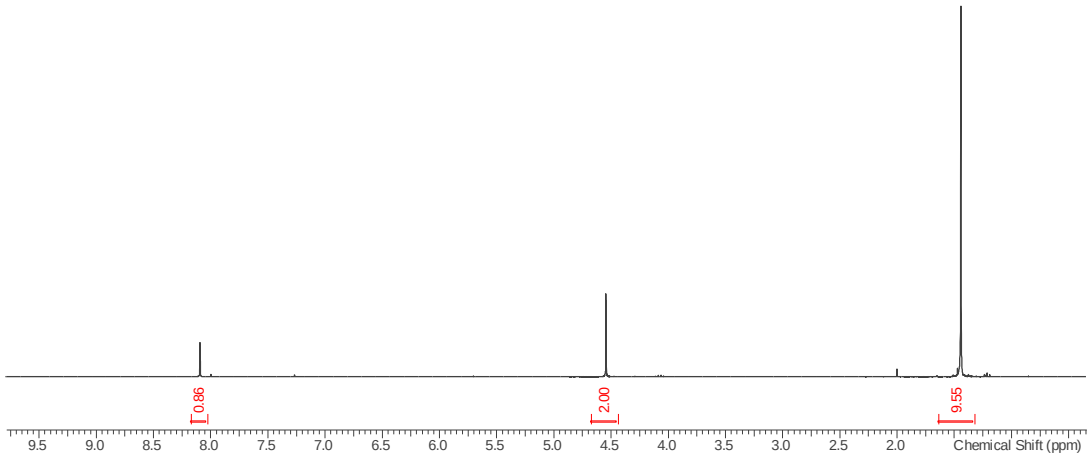


Figure 3.2: NMR spectrum of *tert*-butyl 2-formyloxyacetate

The singlet peak at 1.43 ppm arise from the methyl protons of the *t*-butyl group and singlet peak at 4.53 ppm was from the CH_2 group attached directly to the oxygen atom. The presence of the formate proton at 8.1ppm confirms the structure. The multiplet nature of the peak is due to the coupling of CH_2 protons with the formate proton.

The formic acid part of compound (2) was cleaved to yield *tert* butyl-2- hydroxy acetate (3). This was accomplished by hydrolysis using aqueous $NaHCO_3$ solution. The reaction mixture was stirred overnight at room temperature and the product was extracted into diethyl ether. The liquid product was found to be volatile. Hence evaporation under reduced pressure for a long time would reduce the yield considerably. The structure and purity of the product was verified by NMR spectra as shown in Figure 3.3. Whenever traces of the starting material were observed in the product, the compound was again subjected for hydrolysis until the reaction was completed.

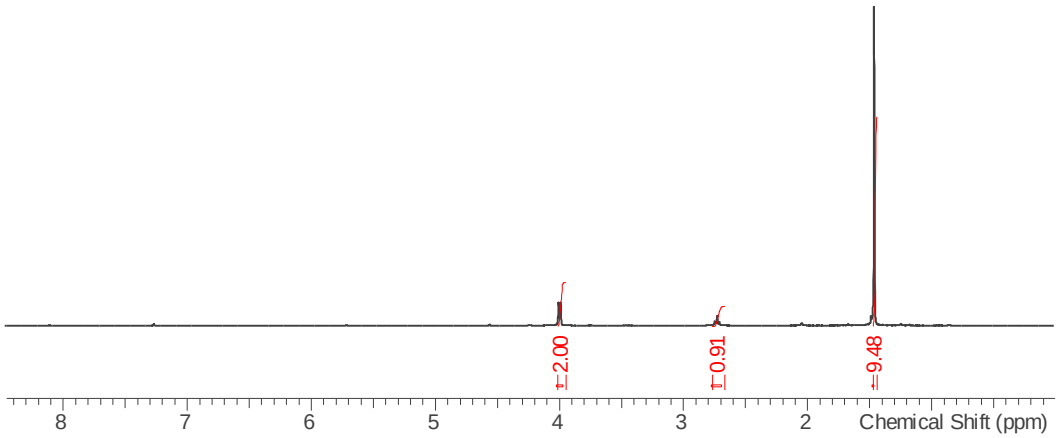


Figure 3.3: NMR spectrum of *tert* butyl-2- hydroxy acetate

Absence of peak at 8.1 ppm indicates that all the formate has hydrolysed. The singlet peak at 1.0 ppm is from the *tert*-butyl group and a doublet peak at 3.98-4.0 ppm was from CH_2 protons. The splitting of the peak was due to interaction of the hydroxyl proton with the CH_2 protons.

3.1.2 Synthesis of Carboxymethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate

The scheme for the synthesis of Carboxymethyl Ethyl 1, 2-Methano [60] fullerene-61, 61-dicarboxylate is drawn in the Figure 3.4 [63]

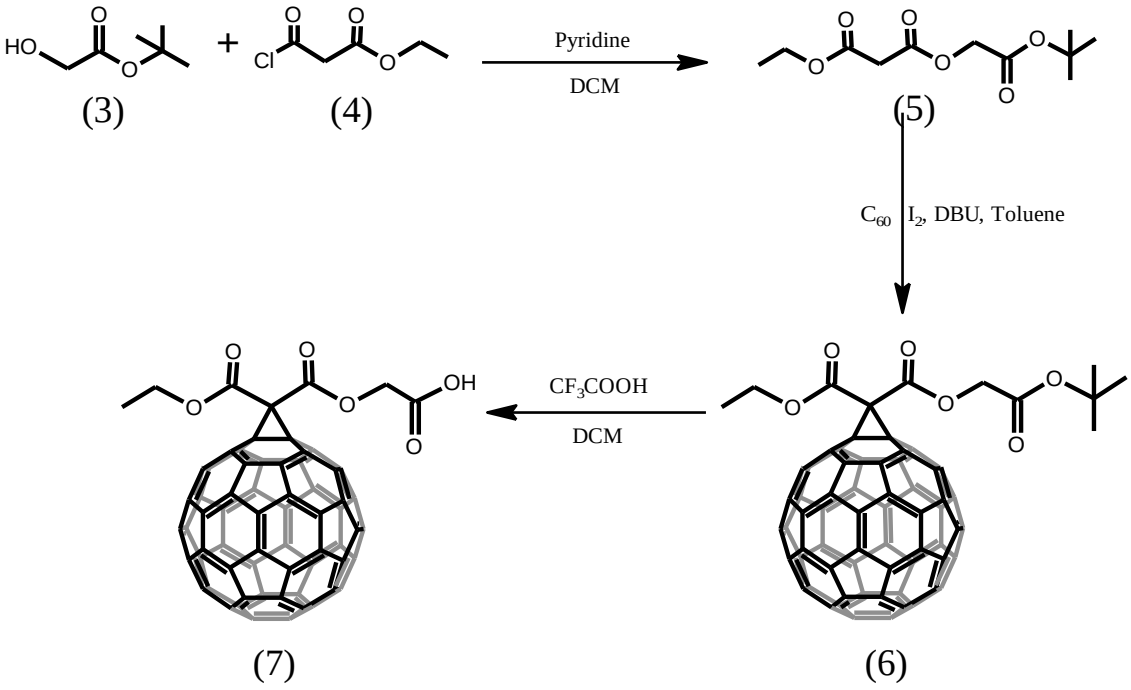


Figure 3.4: Scheme for the synthesis of Carboxy methyl Ethyl 1, 2-Methano [60] fullerene-61, 61-dicarboxylate

The linker (*tert*-Butoxy)-2- oxoethyl Ethyl propanedioate (5) was synthesized from the already prepared intermediate *tert*-butyl hydroxy acetate (3). To a solution of (3) and pyridine in dichloromethane (DCM) kept at 0°C under argon atmosphere, Ethyl 3-chloro-3-oxopropanoate (4) was added and stirred at room temperature for 7 hours. Completion of the reaction was checked by TLC (Hexane/EtOAc: 5/1). Organic phase was washed with saturated NH_4Cl solution, dried over anhydrous Na_2SO_4 to yield compound (5). The product formation was confirmed from the NMR spectra of (5) shown in Figure 3.5

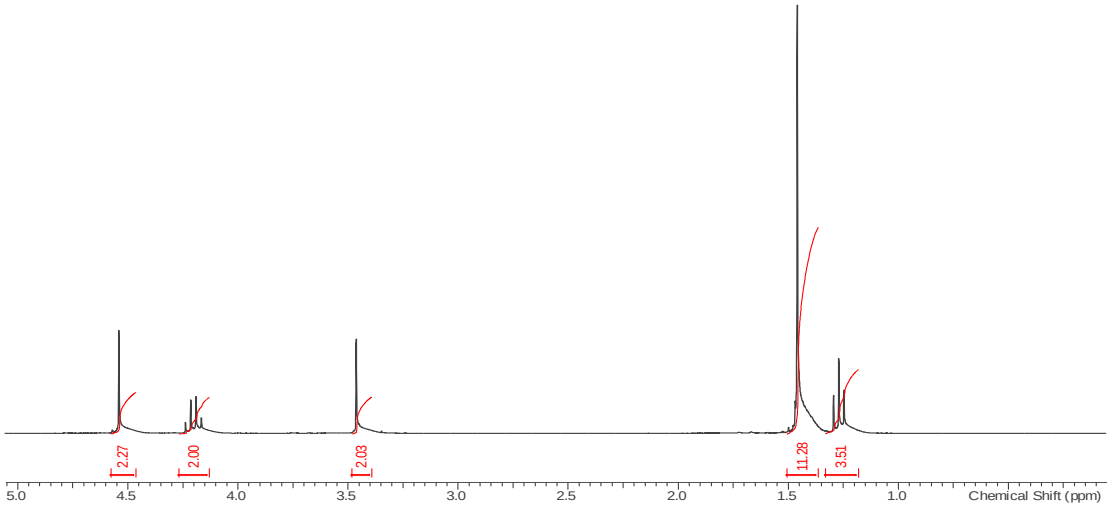


Figure 3.5: NMR spectrum of (*tert*-Butoxy)-2- oxoethyl Ethyl propanedioate

The singlet peak at 4.54 ppm was from the CH_2 protons attached between malonate oxygen and acetate carbonyl group and quartet peaks at 4.16- 4.23 ppm arise from the coupling of methyl group CH_2 protons. The singlet peak at 3.46 ppm was from the CH_2 protons between the malonate carbonyls. The highest intensity peak of the spectrum at 1.45 ppm was from *t*-butyl group and lastly triplet at 1.2 ppm was from methyl protons attached to CH_2 group.

The linker (5) was attached to the fullerene molecule by Bingel reaction in the presence of iodine crystals and base 1, 8-Diazabicyclo [5.4.0] undec-7-ene (DBU). After the completion of reaction by TLC, solvent was evaporated under reduced pressure and at temperature below 40°C. Compound was purified by column chromatography using silica 100 as stationary phase and toluene as eluent to yield the 2-(*tert*- Butoxy)-2-oxoethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (6) as dark red solid. The structure of the compound was confirmed by proton NMR and ESI-TOF mass spectroscopy as shown in Figure 3.6 and Figure 3.7 respectively.

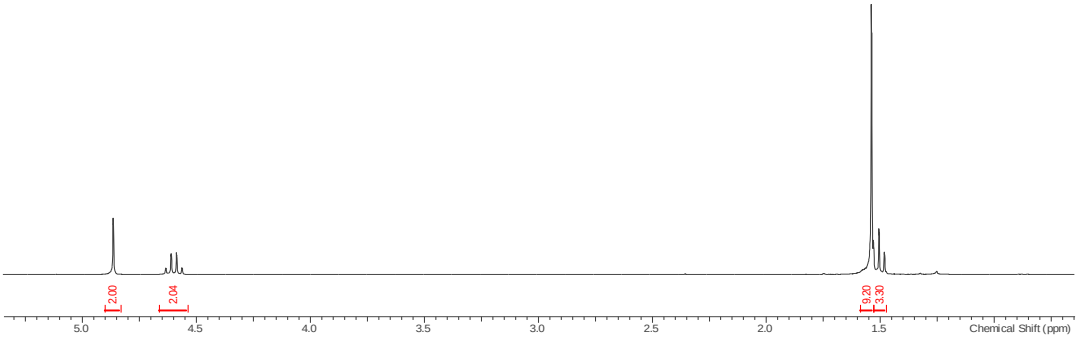


Figure 3.6: NMR spectrum of 2-(*tert*- Butoxy)-2-oxoethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate

From the NMR spectrum, the triplet peak between 1.47 and 1.53ppm corresponds to the terminal methyl of ethoxy group and a singlet peak at 1.54 ppm corresponds to *t*-butyl group. Quartet peaks at 4.56-4.61 ppm correspond to the CH_2 group of ethyl ester. The singlet peak at 4.63 arises from the methylene protons next to the *t*-butoxy carbonyl group. The absence of the singlet peak of malonate CH_2 protons in the spectrum when compared to that described in the figure 5 indicate the attachment of fullerene at that position.

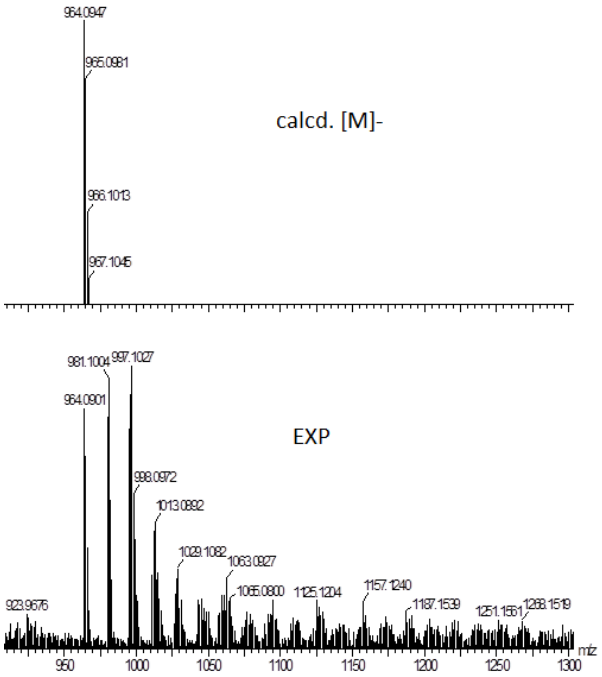


Figure 3.7: ESI-TOF Mass spectrum of Compound (6)

The MS measurement was carried out in negative mode. The $(M)^-$ peak was observed at m/z 964.0901 with accuracy of 4.77 ppm (Lock mass 554.2615)

The synthesis of carboxy methyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate (7) was accomplished by the de-protection of tert butoxy group by trifluoroacetic acid (TFA) in dichloromethane. Upon completion, the reaction mixture was diluted and washed with water and evaporated under reduced pressure to a minimum volume. The solution was dried out on a watch glass and washed with pentane to yield the compound (7). The product was verified both by NMR and mass spectroscopy. The Figure 3.8 presents the NMR spectrum of compound (7).

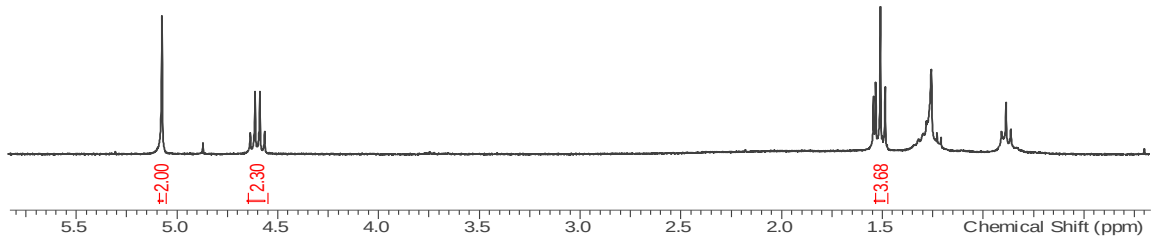


Figure 3.8: NMR spectrum of Carboxy methyl Ethyl 1, 2-Methano [60] fullerene-61, 61-dicarboxylate

The deprotection of the *tert*-butyl group can be confirmed by the absence of characteristic high intensity singlet peak at 1.5ppm. The triplet peak at 1.48 to 1.53 ppm for CH_3 group and quartet peaks for CH_2 group at 4.56-4.63 were still present. However the position of singlet CH_2 peak was slightly shifted from 4.86 to 5.07. This change is due to the fact that, the electron negativity of carbonyl group is increased owing to the transformation from ester to acid.

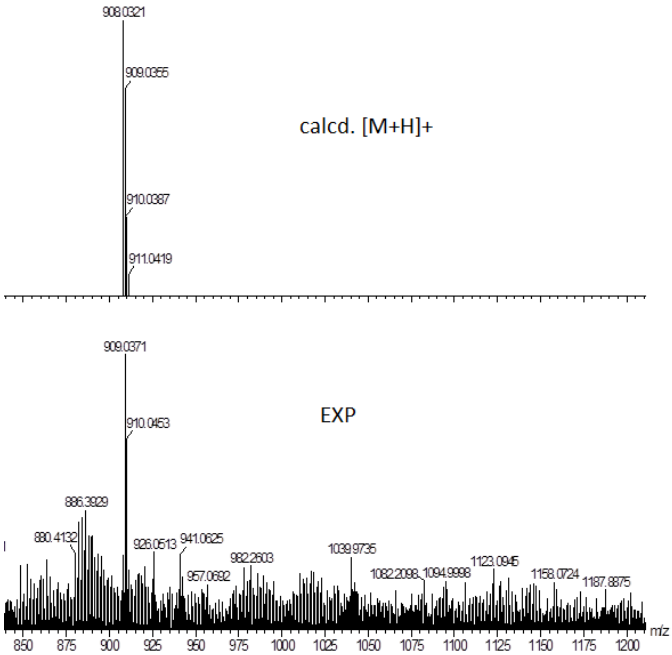


Figure 3.9: ESI-TOF Mass spectrum of Carboxy methyl Ethyl 1, 2-Methano [60] fullerene-61, 61-dicarboxylate

The spectrum in the Figure 3.9 shows the molecular ion measured in positive mode with an accuracy of 3 ppm. The peak observed is the $(M+H)^+$ at m/z 909.0371.

3.1.3 Bis (carboxymethyl) 1,2-Methano[60]fullerene-61,61-dicarboxylate

The synthetic route for the preparation of bis (carboxymethyl) 1,2-methano[60]fullerene-61,61-dicarboxylate is shown in the Figure 3.10. The scheme follows the protocol similar to the one described earlier for the synthesis of compound (7). [63]

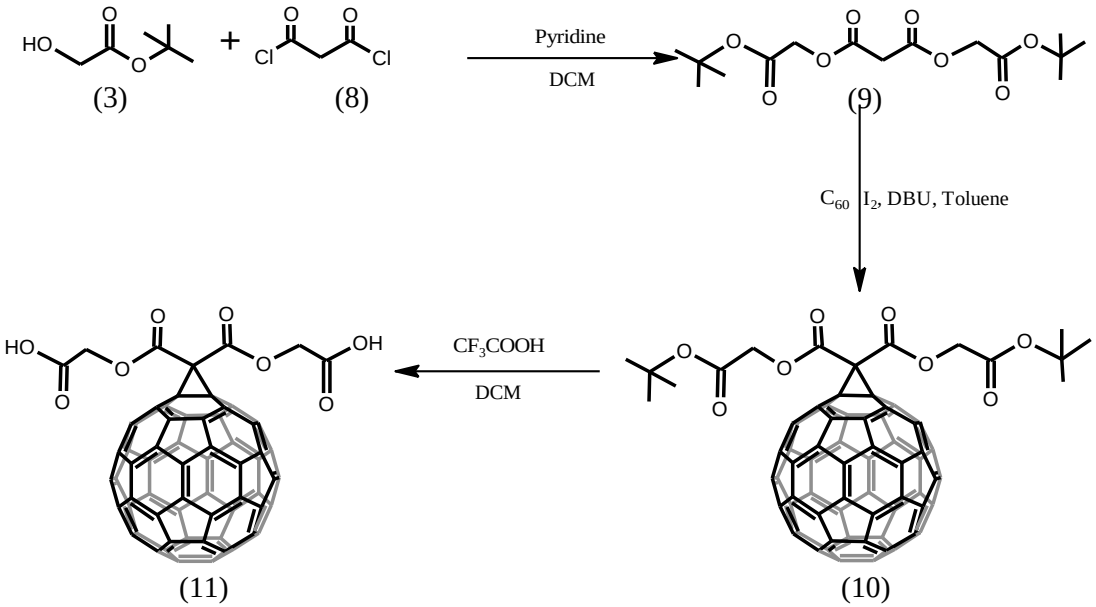


Figure 3.10: Scheme for the synthesis of Bis (carboxymethyl) 1,2-Methano[60]fullerene-61,61-dicarboxylate

The intermediate bis [2- (*tert*- butoxy-2-oxoethyl)] propanedioate (9) was synthesized from compound (3). Commercially available malonyl dichloride (8) was coupled with compound (3) in the presence of base pyridine by stirring at room temperature for 18 hours. After the completion of the reaction, the organic layer was washed with water and evaporated under reduced pressure to yield dark green syrup. The compound was purified by column chromatography with silica100 as stationary phase and ethyl acetate in hexane as eluent to get product (9) as colourless liquid.

The ^{1}H NMR spectrum of the compound is shown in Figure 3.11

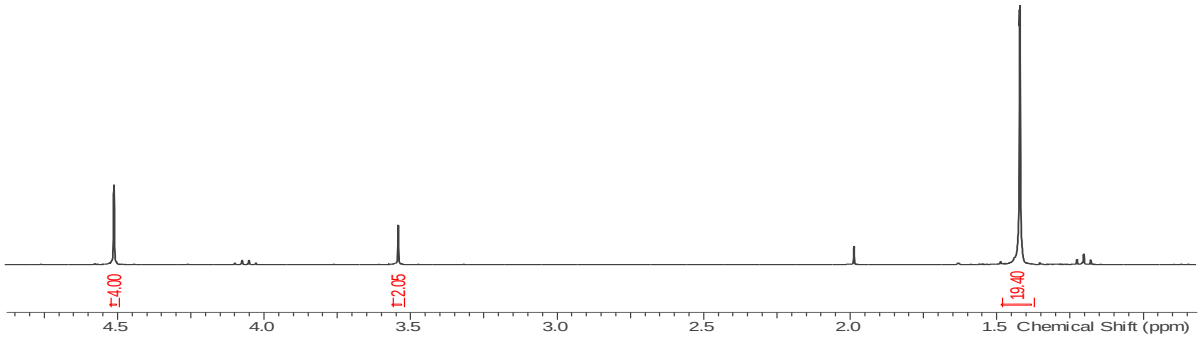


Figure 3.11: 1H NMR of Bis [2- (*tert*- butoxy-2-oxoethyl)] Propanedioate

The ^{1}H NMR spectrum of the compound contains a characteristic high intensity singlet peak of *tert*- butyl group at 1.42 ppm. Since the compound is symmetrical, the singlet peak represents *t*-butyl groups at the both ends of the molecule. The CH_2 protons of the malonate give rise to a singlet peak at 3.54 ppm and again due to the symmetrical nature of the molecule there is only one peak at 4.51 ppm for CH_2 protons between malonate oxygen and *tert*-butoxy carbonyl group.

The compound (9) was attached to fullerene by Bingel reaction using the similar reaction conditions as mentioned in the synthesis of (6). The compound was isolated and purified by column chromatography using silica 100 and toluene as eluent to yield bis [2- (*tert*- butoxy-2-oxoethyl)]1,2-methano[60]fullerene-61,61-dicarboxylate (10) as a dark solid. The structure of the compound was established by NMR and mass spectroscopy. Figure 3.12 shows the NMR spectrum of the compound.

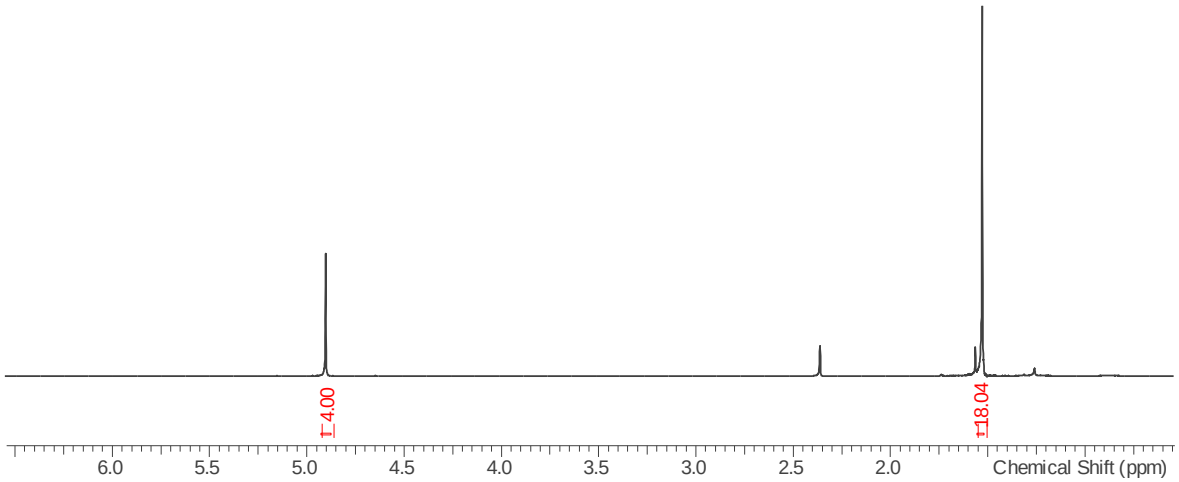


Figure 3.12: NMR spectrum of Bis [2- (*tert*- butoxy-2-oxoethyl)]1,2-Methano[60]fullerene-61,61-dicarboxylate

The singlet peak at 4.9 ppm corresponds to the methylene proton next to malonate ester and the singlet peak at 1.52 ppm arises from the methyl protons of *tert*- butyl groups. The most important detail that can be drawn from the spectra is the absence of singlet peak at 3.2 ppm when compared with the precursor compound (9). This is the

proof that the linker molecule is connected to the fullerene at the malonate CH_2 position.

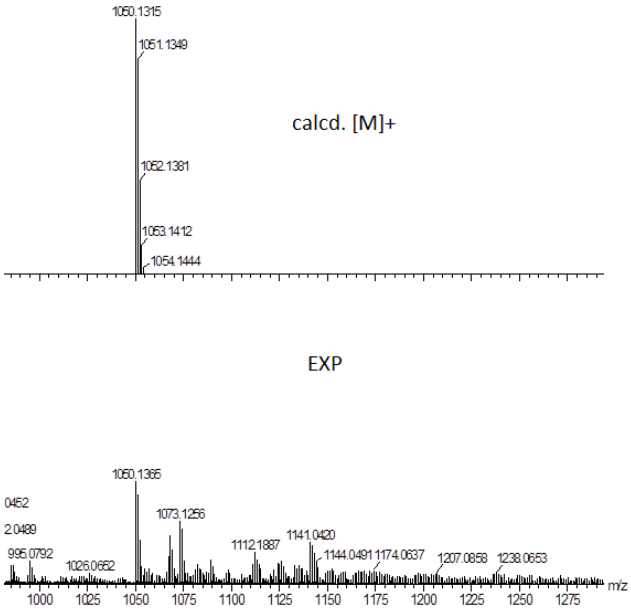


Figure 3.13: ESI-TOF Mass spectrum of Bis [2- (*tert*- butoxy-2-oxoethyl)]1,2-Methano[60]fullerene-61,61-dicarboxylate

Structure the compound was confirmed by ESI-TOF mass spectroscopy as shown in the Figure 3.13 with an accuracy of 4.8 ppm. The mass peak appeared as $(M)^+$ at m/z value 1050.1365

Bis (carboxymethyl) 1,2-methano[60]fullerene-61,61-dicarboxylate(11) was synthesized by the removal of *tert*-butyl groups attached to the Compound (10) using TFA in DCM. As per the TLC shown in Figure 3.14 ($CHCl_3$/EtOH: 18/1), the starting material was found to be consumed after 1st hour of addition to produce a mixture of presumably mono and di-acid. However, the complete deprotection of the second ester group was achieved only after 16 hours. Owing to the poor solubility of the compound, MS and NMR analysis was not possible to perform.

Figure 3.14: TLCs showing the disappearance of starting material and monoacid.

3.2 Fullerenes with Thioacetate anchors

3.2.1 Synthesis of 2-(acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate.

The scheme for the synthesis of 2-(acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate (16) is shown in Figure 3.15

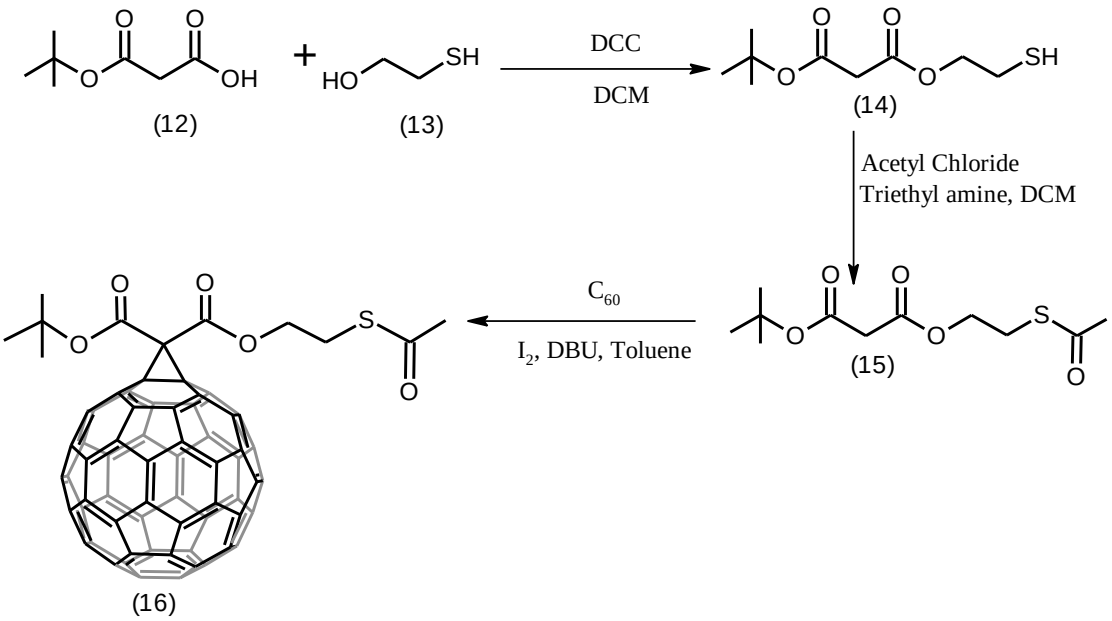


Figure 3.15: Scheme for the synthesis of 2-(acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate.

The synthesis of the intermediate *tert*-butyl 2-Mercapto ethyl Malonate (14) is achieved by coupling mono *tert*-butyl malonate(12) and mercapto ethanol in DCM using 1,3-dicyclohexylcarbodiimide (DCC) at room temperature. The target compound was purified by column chromatography. [64]

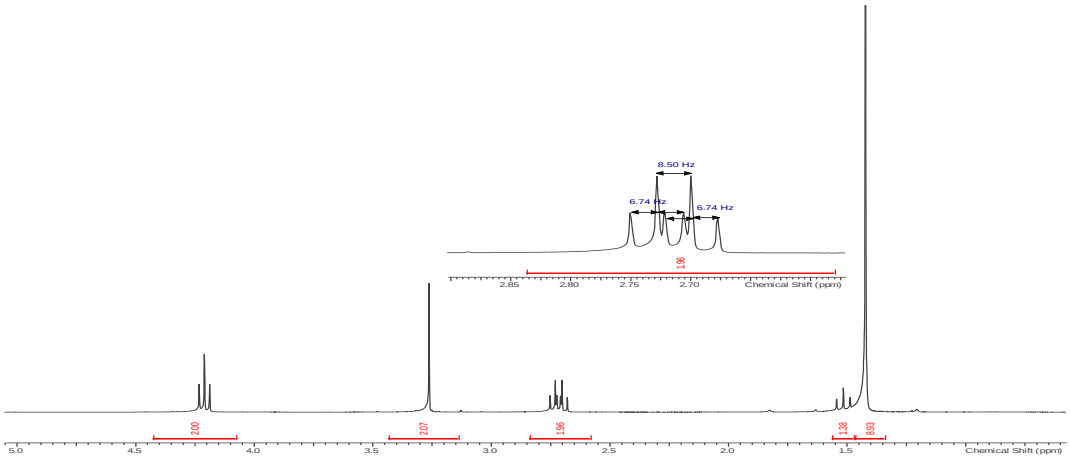


Figure 3.16: 1H NMR spectrum of *tert*-butyl 2-Mercapto ethyl Malonate

The spectrum in the Figure 3.16 shows a triplet peak at 4.21 ppm which corresponds to the CH_2 protons between malonate ester and thiol methylene. The malonate protons appear as a singlet peak at 3.26 ppm and the CH_2 protons adjacent to the SH group are visible as multiplet at 2.68-2.75 ppm. In fact, even though the peak appears as a multiplet, close examination reveals that it is actually an overlapping doublet of triplets with coupling constants 8.50 Hz and 6.74 Hz respectively. The coupling of CH_2 group with the adjacent thiol proton and nearby methylene protons gives rise to this multiplet appearance. The triplet peak of SH proton at 1.5 ppm with coupling constant 8.50 Hz confirms the above mentioned argument. The nine *tert*-butyl protons produce a singlet peak at 1.46 ppm.

The position of the thiol proton in the ^1H NMR spectra is resolved with the help of COSY spectrum shown in Figure 3.17.

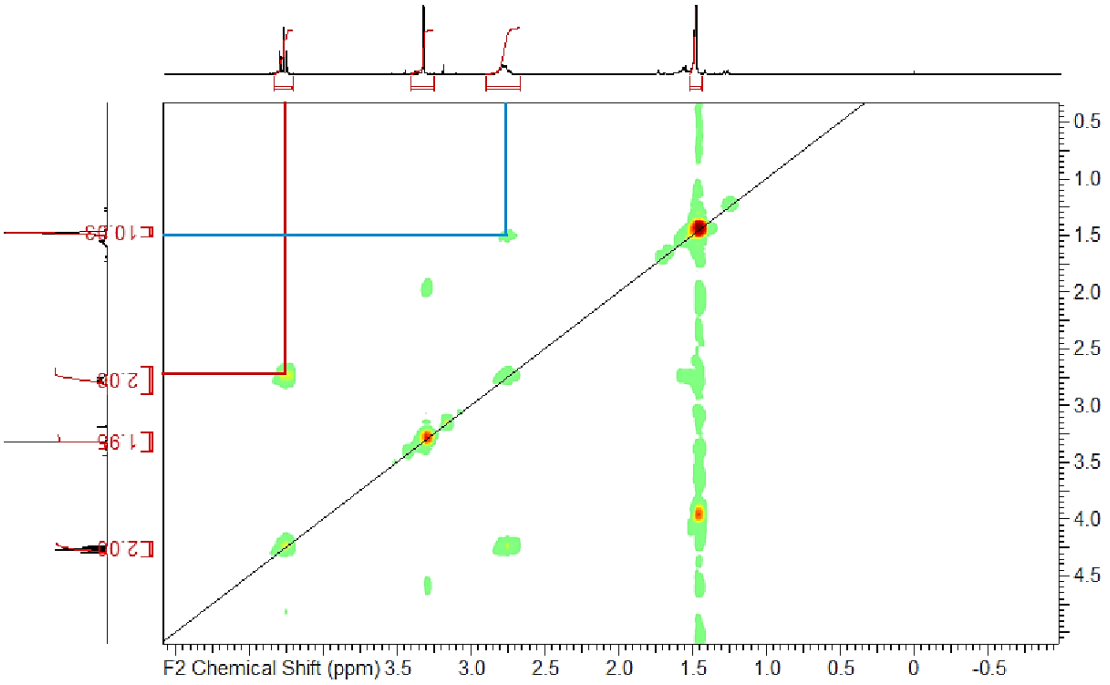


Figure 3.17: Cosy spectrum of *tert*-butyl 2-Mercapto ethyl Malonate

In the Figure 3.17, the peaks connected by red line indicate the coupling interaction between the CH_2 protons next to malonate ester and its adjacent methylene group. That is the reason why triplet signal is observed at 4.21 ppm for 2 protons. Since the methylene group is in between CH_2 protons and sulphur atom, the blue line in the figure reveals that thiol proton signal should appear somewhere near the *tert*-butyl protons at 1.42 ppm. Thus the triplet peak seen at 1.5 ppm with coupling constant 8.50 Hz is confirmed to be that of thiol proton beyond any doubts.

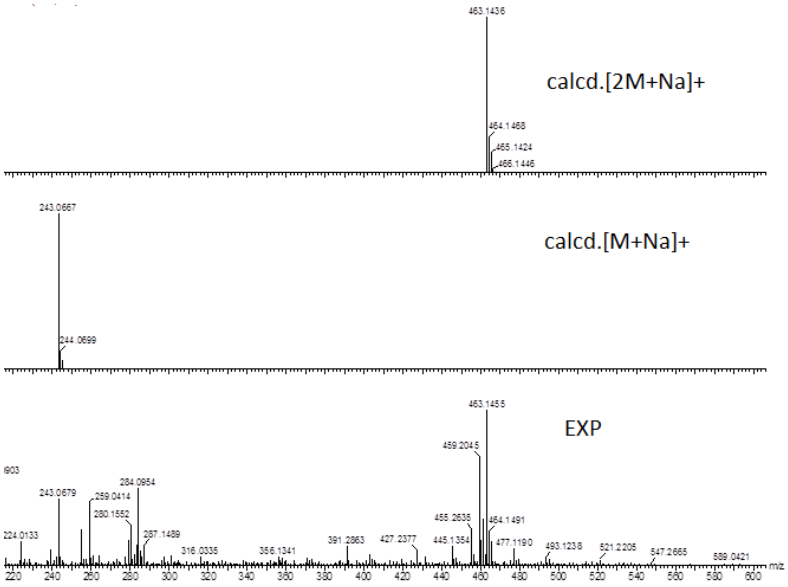


Figure 3.18: ESI-TOF Mass spectrum of *tert*-butyl 2-Mercapto ethyl Malonate

ESI-TOF mass spectrum in positive mode shown in Figure 3.18 confirms the molecular mass of the compound. The $(M+Na)^+$ is observed at m/z value 243.0679 (Lock mass 557.2802) with an accuracy of 5 ppm and $(2M+Na)^+$ is visible at m/z value 463.1455 with an accuracy of 4 ppm.

The free thiol group of the compound (14) was converted to thioacetate by reacting with acetyl chloride in DCM in the presence of triethyl amine in a sealed vial. After consumption of starting material by TLC (hexane/EtOAc: 7/3), reaction mixture was washed with water to remove the triethylamine salt, dried over anhydrous sodium sulphate and evaporated under reduced pressure. The mixture was purified by column chromatography and concentrated fractions were collected and evaporated under reduced pressure to give 2-(acetylsulfanyl) ethyl *tert*-butyl malonate (15)

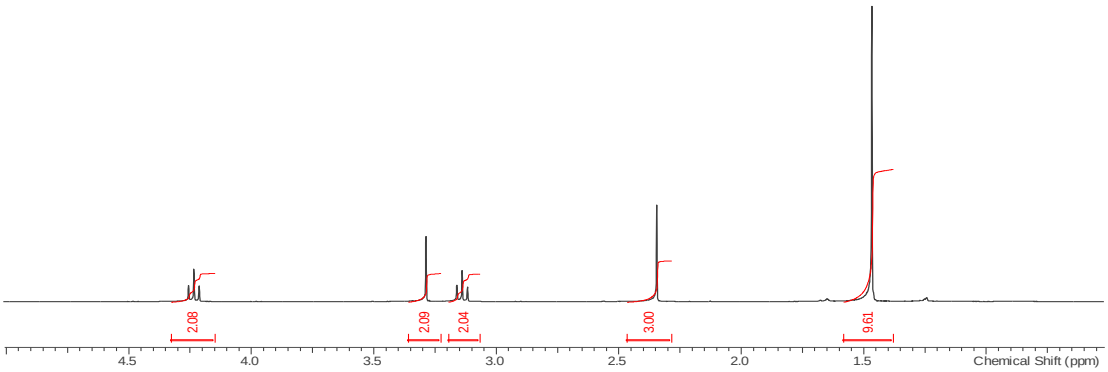


Figure 3.19: ^{1}H NMR spectrum of 2-(acetylsulfanyl) ethyl *tert*-butylMalonate

Even though, only difference between the precursor and the product compound is the attachment of acetyl moiety to the thiol functional group, the spectrum (Figure 3.19) has some notable differences. Important one is the appearance of acetyl protons as a singlet peak at 2.34 ppm. The triplet thiol proton at 1.5 ppm is absent in this spectrum and the multiplet 2.68-2.75 ppm has changed to a triplet peak, however at higher 3.14 ppm. The remaining peaks in the spectrum are triplet peaks at 4.23 corresponding to CH_2 protons next to malonate ester, singlet peak at 3.28 ppm corresponding to malonate protons.

The 2-(acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate (16) was synthesized by attaching the (15) to fullerene by Bingel reaction using the similar conditions described in the previous chapter. The pure product obtained after purification by column chromatography (Silica ge100; Eluent $CHCl_3$) was identified by NMR and mass spectroscopy.

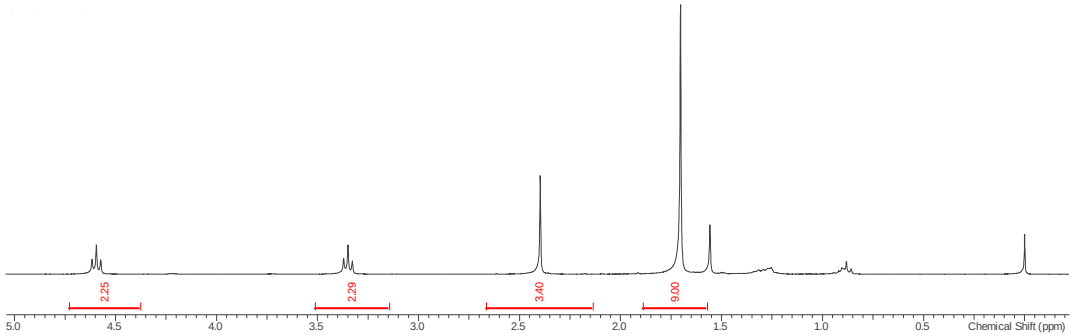


Figure 3.20: 1H NMR of 2-(acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate

The spectrum in Figure 3.20 is almost similar to the starting material used. However the malonate protons at 3.28 ppm are absent, which indicate that fullerene is attached to the molecule at this position replacing the protons. Appearance of the remaining peaks holds the same explanation as that in the previous spectrum.

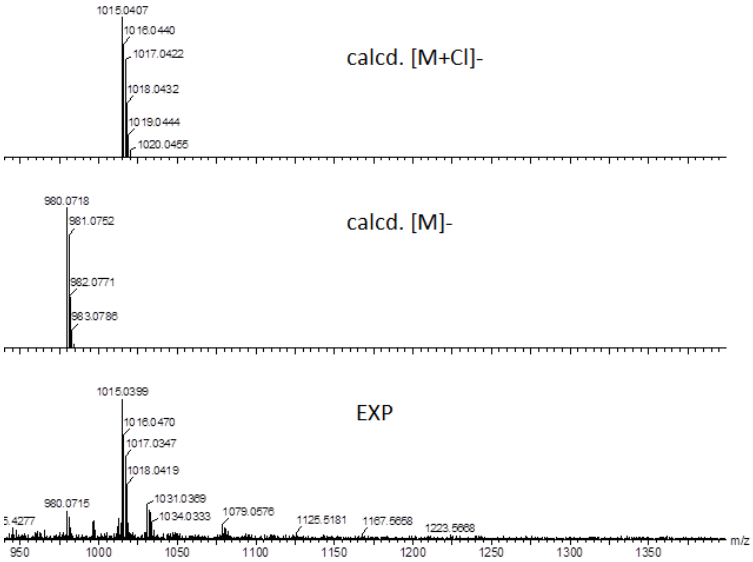


Figure 3.21: ESI-TOS mass spectra of 2-(acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate

The ESI-TOF mass measurement (Figure 3.21) was carried out in negative mode with lock mass 555.2645. The target mass is observed at m/z value 980.0715 which corresponds to $(M)^-$ with an accuracy of 0.5 ppm and at 1015.0399 corresponding to $(M+Cl)^-$ with an accuracy of 0.8 ppm

3.2.2 Synthesis of 3-(acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate

The synthesis of 3-(acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate is carried out using the following sequence mentioned in Figure 3.22.

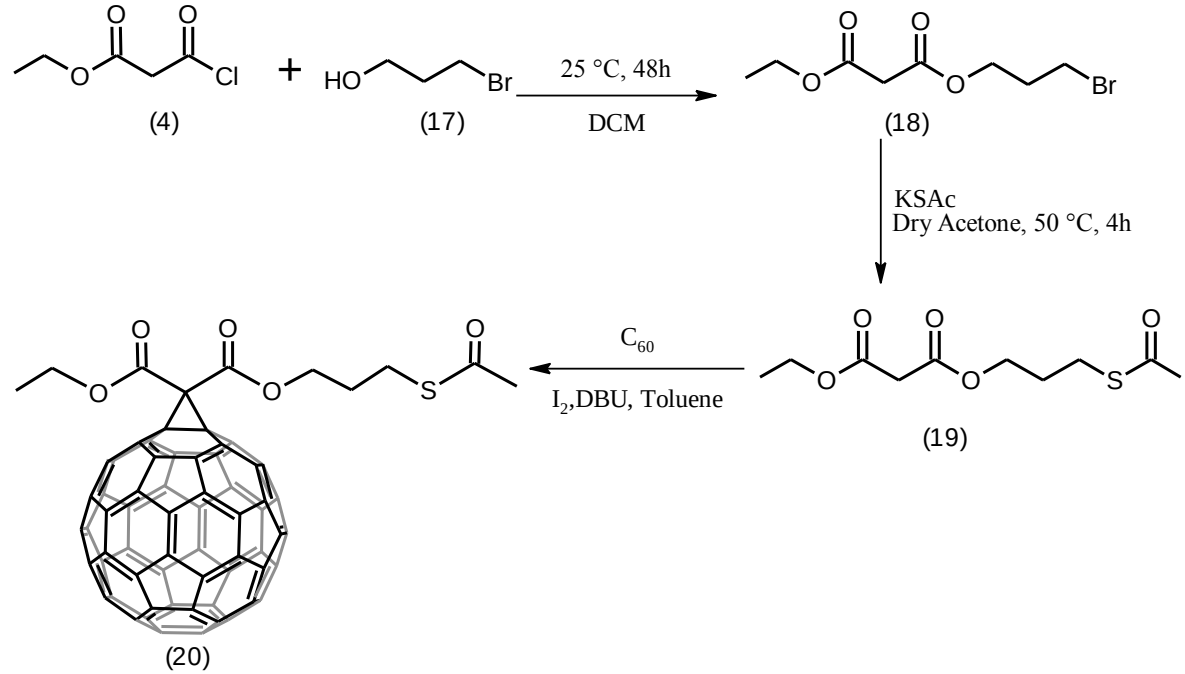


Figure 3.22: Scheme for the synthesis of 3-(acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate

3-Bromo propyl ethyl malonate (18) was synthesized by coupling commercially available ethyl malonyl chloride (4) and 3-bromo propanol (17) by stirring in a sealed vial for 48 hours at room temperature. The product formed was purified by column chromatography using silica100 and 10% EtOAc in hexane and identified by NMR spectroscopy.

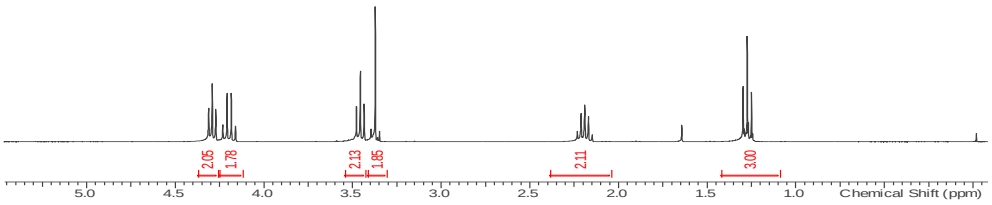


Figure 3.23: ^{1}H NMR spectrum of 3-bromo propyl ethyl malonate (18)

In Figure 3.23, CH_2 protons next to the malonate ester and methylene group appear as triplet peak at 4.27-4.31ppm and the CH_2 protons attached to the other end of the malonate are visible as quartet signal at 4.16-4.23 ppm. The triplet peak at 3.43-3.48 ppm corresponds to methylene protons attached to bromine atom. The singlet peak at 3.37 ppm originates from malonate protons and the methylene protons next to O-CH_2 and Br-CH_2 group appear as a quintet at 2.15-2.23 ppm. Finally the methyl protons give the signal as triplet at 1.25-1.30 ppm.

The compound (18) was coupled with potassium thioacetate (KSAc) by heating at 50°C for 4 hours in dry acetone. After completion of the reaction, the byproduct formed was filtered off and compound was purified by column chromatography (Silica gel 100; 18% EtOAc in hexane) to yield pure product of [3-(acetylsulfanyl) propyl] ethyl malonate (19).

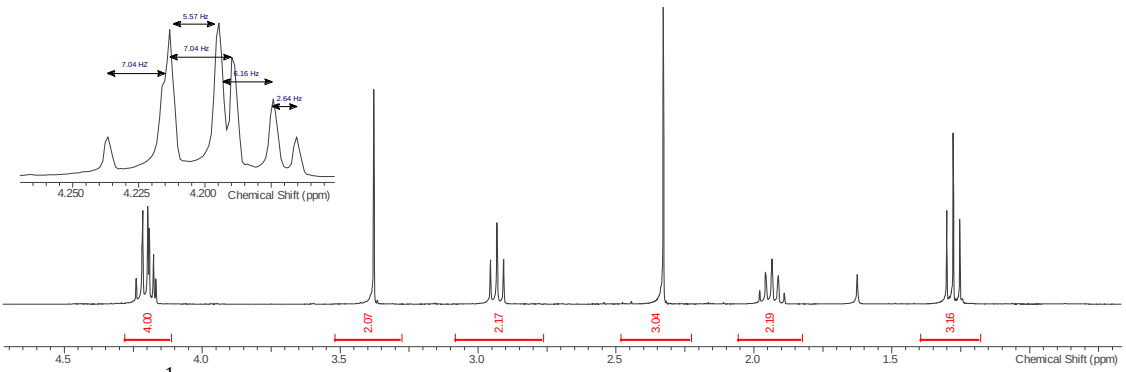


Figure 3.24: ^{1}H NMR spectrum of [3-(acetylsulfanyl) propyl] ethyl malonate (19)

In Figure 3.24, the triplet and quartet peaks corresponding to the CH_2 protons attached to the both ends of malonate ester overlap to form a multiplet appearance at 4.17- 4.24 ppm. The singlet peak at 3.38 is from the malonate methylene group and triplet peak at 2.90 to 2.95 ppm corresponds to CH_2 protons next to sulphur atom. The singlet peak at 2.33 ppm orginates from acetyl group and quintet peak at 1.89-1.98 is from CH_2 protons next to O-CH_2 and SAc-CH_2 group. The methyl group generates the triplet peak at 1.25-1.30 ppm.

The synthesis of 3-(acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate (20) was carried out by coupling fullerene with compound (19) by bingel reaction. The reaction conditions were similar to those mentioned in the previous chapters. The compound was purified by column chromatography using silicagel 100 and toluene/$CHCl_3$ as eluent.

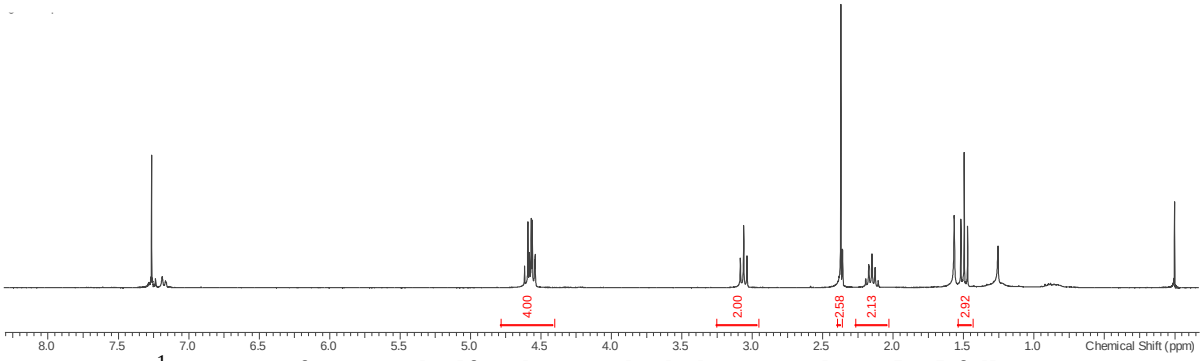


Figure 3.25: ^{1}H NMR of 3-(acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate

The spectrum in the Figure 3.25 holds most of the characteristic peaks of the precursor compound (19). The notable difference is absence of the malonate protons (at 3.38 ppm) from the spectrum. The multiplet peak at 4.56 corresponds to the overlapping of CH_2 protons attached malonate protons, triplet signal at 3.06 ppm arises from the methylene protons adjacent to the sulphur atom and the singlet peak at 2.37 ppm is from the acetyl protons. The CH_2 protons between the O-CH_2 and SAc-CH_2 produce quintet signal at 2.1 ppm and lastly the triplet peak at 1.45 ppm is from splitting of the methyl protons by nearby CH_2 protons.

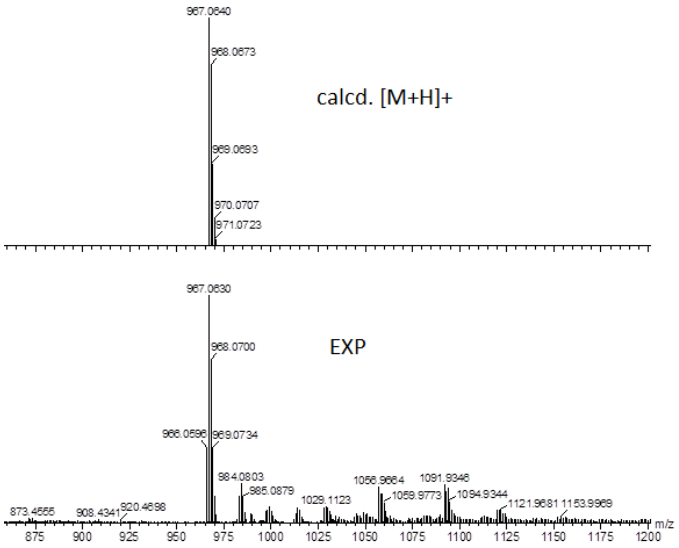


Figure 3.26: ESI-TOF mass spectrum of 3-(acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate

The mass measurement (spectra shown in Figure 3.26) was done in positive mode with lock mass 557.2802 and the targeted mass is identified as $(M+H)^+$ at m/z value 967.0630 with an accuracy of 1.03 ppm.

3.3 Fullerene with thiol and disulphide anchor

3.3.1 Bingel reaction with unprotected thiol

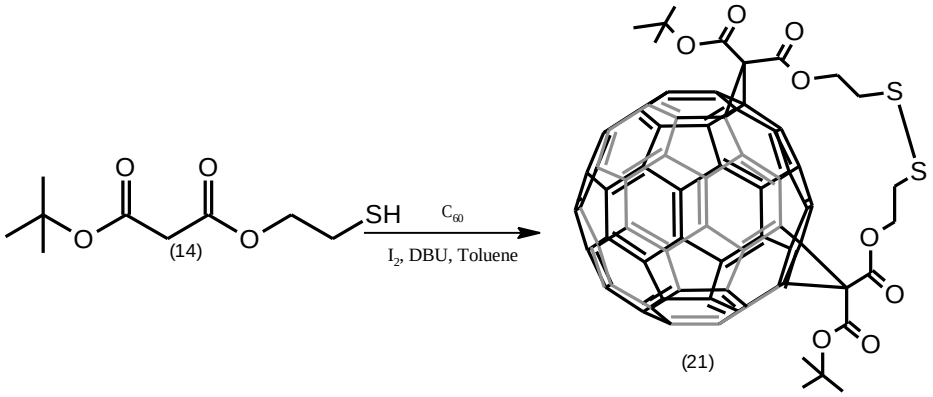


Figure 3.27: Bingel reaction with unprotected thiol group

Bingel reaction with unprotected thiol group was carried out using iodine and base DBU (Figure 3.27). However the reaction did not produce the desired mono-C60 adduct. Instead formation of disulphide fullerene adduct was observed. Presence of iodine in the reaction mass might have favored the disulphide bond formation. The product was isolated by column chromatography and verified by MS spectroscopy (Figure 3.27).

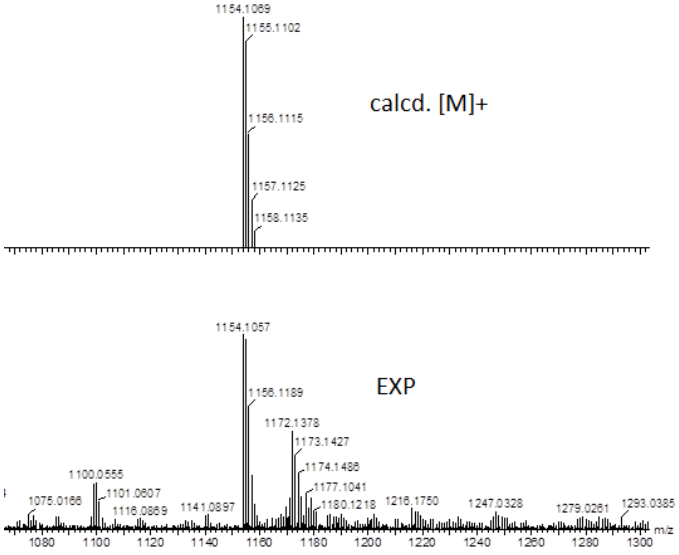
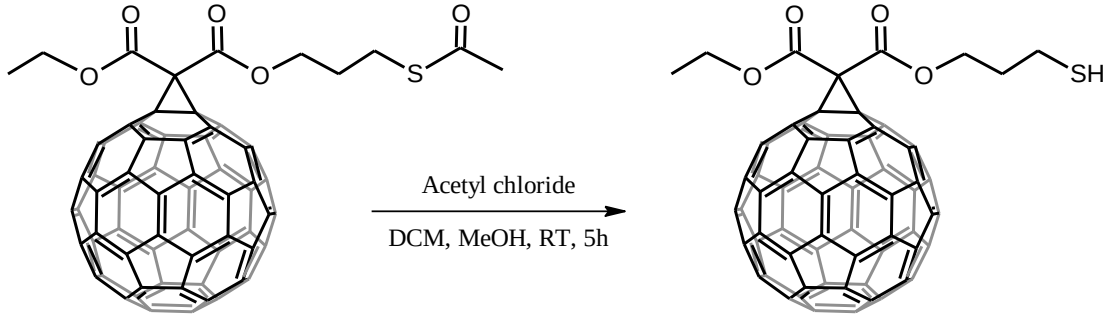


Figure 3.28: ESI-TOF Mass spectrum of C_{60}-bisulfide adduct

ESI-TOF mass spectrometry in positive mode with lock mass 557.2802 confirmed the product at m/z value 1154.1057 as $(M)^+$ with accuracy 1.03 ppm. The spectrum is shown in the Figure 3.28.

3.3.2 Synthesis of Ethyl (3-Sulfanyl propyl) 1,2-Methano[60] fullerene-61, 61-dicarboxylate

The scheme for the synthesis of ethyl (3-sulfanyl propyl) 1, 2-methano [60] fullerene-61, 61-dicarboxylate (22) is shown in the Figure 3.29.



(20) (22)

Figure 3.29: Scheme for the synthesis of ethyl (3-sulfanyl propyl) 1, 2-methano [60] fullerene-61, 61-dicarboxylate

Ethyl (3-sulfanyl propyl) 1, 2-methano [60] fullerene-61, 61-dicarboxylate (22) was synthesized by the cleavage of thioacetate group by stirring with acetyl chloride in a 15:1 ratio mixture of DCM and methanol at room temperature under under inert atmosphere. Reaction mixture was washed with water and purified by column chromatography to yield pure product of (22). [65]

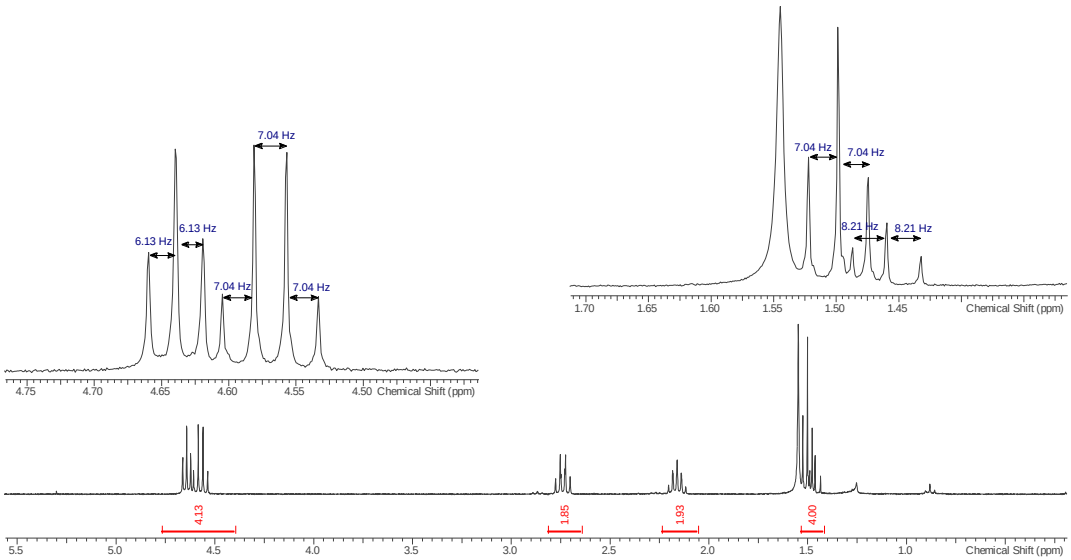


Figure 3.30: ^{1}H NMR spectrum of ethyl (3-sulfanyl propyl) 1, 2-methano [60] fullerene-61, 61-dicarboxylate

The multiplet peak at 4.53-4.66 ppm in the spectrum (Figure 3.30) corresponds to four methylene protons attached to the either ends of malonate oxygen. Upon close examination reveals that the multiplet is actually an overlap of triplet and quartet peaks with coupling constant 6.13 and 7.04 Hz respectively. The quartet peak at 2.70-2.77 ppm arises from the CH_2 protons next to the thiol group and quintet peak is from the CH_2 protons between O-CH_2 and SAc-CH_2 group.

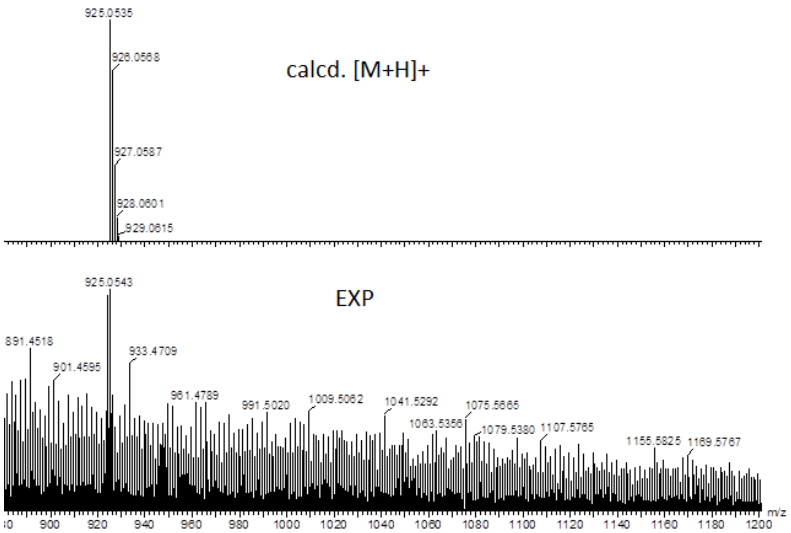


Figure 3.31: ESI-TOF Mass spectrum of Ethyl (3-Sulfanyl propyl) 1, 2-Methano [60] fullerene-61, 61-dicarboxylate

The ESI-TOF mass spectroscopy (Figure 3.31) was measured in positive mode with lock mass 557.2802 and the peak of the compound was found at m/z 925.0543 as $(M)^{+}$ with 0.86 ppm accuracy.

4 EXPERIMENTAL PART

4.1 General

Solvents and reagents used for the synthesis were purchased from Merck, Sigma-Aldrich and VWR international and used as received without further purification unless otherwise mentioned. Chloroform and dichloromethane were distilled over anhydrous potassium carbonate, acetone over P_2O_5 to ensure they are completely moisture free. Ready to use aluminum sheet coated silica gel 60 F_{254} TLC plates purchased from Merck were used for monitoring the reactions. Depending on the polarity of the compounds to be separated, purification by column chromatography were performed either using silica gel 60 (mesh size 40-63µm) or silica gel 100 (63-200µm) from Merck.

NMR measurements were carried out using Varian Mercury 300 MHz spectrometer (Varian Inc.) and chemical shifts were calculated in ppm with respect to tetramethyl silane (TMS) as internal standard. ESI-TOF LCT premier XE mass spectrometer (Waters corp.) was used for measuring the molecular masses of compounds. The raw data were processed by applying mass correction and isotope modelling was used to calculate the accuracy in the measurements.

4.2 Synthesis

4.2.1 *tert*-Butyl 2-formyloxyacetate (2):

To a solution of formic acid (1.83 g, 0.0394 moles) in 40 mL of ethyl acetate, was added triethylamine (4.21g, 0.041 moles) and the reaction mass was stirred at room temperature for 5minutes. *tert*-Butylbromoacetate (5g, 0.0256 moles) was added and the reaction mixture was stirred for another 16 hours. The precipate formed was filtered off and washed with 100 mL of diethyl ether. The combined filtrate was washed with 40 mL of half saturated brine solution, dried over anhydrous sodium sulphate and evaporated under reduced pressure to yield a colourless liquid of **(2).** (3.1g, 75%). ^{1}H NMR ($CDCl_3$, 300MHz):1.43 (s, 9H); 4.53 (s, 2H); 8.08 (s, 1H)

4.2.2 *tert* Butyl-2- hydroxy acetate (3):

Sodium bicarbonate (3.14g, 0.0373 moles) was added to *tert*-butyl 2-formyloxy acetate (2.9g, 0.0180 moles) in 57 mL of water and the mixture was stirred at room temperature for 24 h. The product formed was continuously extracted into 50 mL of diethyl ether by stirring for another 24 h. The layers were separated, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to yield **3** as colorless oil (1.6 g, 66.9 %).^{1}H NMR ($CDCl_3$, 300 MHz): 1.45 (s, 9H), 2.7 (t, *J*= 5.28 Hz, 1H), 3.98 (d, *J*= 5.28 Hz, 2H)

4.2.3 (*tert*-Butoxy)-2- oxoethyl ethyl propanedioate (5):

Ethyl 3-chloro-3-oxopropanoate (4) (0.236 g, 0.00157 moles) was added to *tert* butyl-2-hydroxy acetate **(3)** (0.208 g, 0.00157 moles) and pyridine (0.152 mL, 0.00188 moles) in dry dichloromethane (12 mL) at 0°C. The resultant solution was allowed to warm slowly to r.t. over 1 h and stirred for additional 6 h. Progress of the reaction was monitored by TLC (Hexane/EtOAc: 5/1). Upon completion, the reaction was quenched by adding sat. NH_4Cl solution (12 mL) and stirring for 2 minutes. Layers were separated and organic layer was washed with sat. NH_4Cl solution (3x12 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford **5** (0.3875g, 83%) ^{1}H NMR ($CDCl_3$, 300 MHz): 1.24 (t, 3H), 1.45 (s, 9H), 3.46 (s, 2H), 4.16 (q, 2H) 4.54 (s, 2H)

4.2.4 2-(*tert*- Butoxy)-2-oxoethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (6):

Fullerene C_{60} (0.1g, 0.000138 moles) was dissolved in 150 mL of dry toluene under Ar atmosphere under stirring. Iodine crystals (0.03521g, 0.000138 moles) were added to the solution, followed by compound **5** (0.03417g, 0.000138 moles) and DBU (0.0412 mL, 0.000277 moles) and the reaction mass was stirred at room temperature for 5 h. The progress of reaction was monitored by TLC (100% toluene system). The solvent was Evaporated under reduced pressure and the product was purified by using column chromatography (silica gel 100, eluent: toluene) to get **6** dark red solid. (0.0991g, 67%) ^{1}H NMR ($CDCl_3$, 300 MHz) 1.48 (t, 3H), 1.54 (s, 9H), 4.56 (q, 2H), 4.86 (s, 2H); ESI-TOF m/z: calculated for $C_{71}H_{16}O_6$ $(M)^-$, 964.0947; found 964.0901.

4.2.5 Carboxymethyl ethyl 1, 2-Methano [60] fullerene-61, 61-dicarboxylate (7):

Compound **6** was dissolved in dichloromethane (5 mL) and trifluoroacetic acid (2 mL) was added. The progress of the reaction was monitored by TLC (100% toluene). Upon completion, water (10 mL) and dichloromethane (10 mL) were added to the reaction mixture and the layers were separated. Organic layer was washed with water (2 x10 mL), dried over anhydrous Na_2SO_4 and evaporated to minimum volume and was allowed for drying out on a watch glass. The solid product was washed with pentane to yield dark red solid **(7).** (0.063 g, 74%). ^{1}H NMR ($CDCl_3$, 30 0MHz) 1.48 (t, 3H) 4.56 (q, 2H) 5.07 (s, 2H); ESI-TOF m/z: calculated for $C_{67}H_8O_6$ $(M+H)^+$, 909.0399; found 909.0371

4.2.6 Bis [2- (*tert*- butoxy-2-oxoethyl)] Propanedioate (9):

A solution of *tert* butyl-2- hydroxy acetate **(3)** (0.204g, 0.00154 moles) and pyridine (0.236 mL, 0.00154 moles) in dry dichloromethane (3 mL) was purged with argon gas and cooled to 0°C. To the resultant solution, malonyl dichloride (8) (0.075 mL, 0.0007 moles) was added. After stirring at 0°C for 2.5 hours, the cooling bath was removed

and stirring was continued for another 16 hours at room temperatureThe progress of the reaction was monitored by TLC ($CHCl_3$/EtOH: 9/1). Reaction was quenched by adding water and the layers were separated. Organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get dark green syrup. The compound was purified by column chromatography (eluent 20% EtOAc in hexane) to yield **(9)** as colorless liquid (0.090 g, 18%). ^{1}H NMR ($CDCl_3$, 300MHz): 1.42 (s, 18H), 3.54(s, 2H), 4.51(s, 4H).

4.2.7 Bis [2- (*tert*- butoxy-2-oxoethyl)] 1, 2-Methano [60] fullerene-61, 61-dicarboxylate (10):

Fullerene C_{60} (0.0976g, 0.000138 moles) was dissolved in 150 mL of dry toluene under argon atmosphere. Iodine crystals (0.03437g, 0.000138 moles) were added, followed by **9** (0.0450g, 0.000138 moles) and DBU (0.0412 mL, 0.000277moles) and the reaction mixture was stirred at room temperature for 5 hours. The progress of the reaction was monitored by TLC (100% toluene system). The product was purified by column chromatography (silica gel 100, eluent: toluene) and washed with pentane to get **10** as dark red solid. (0.085g, 60%).^{1}H NMR ($CDCl_3$, 300MHz): 1.52(s, 18H), 4.90(s, 4H); ESI-TOF m/z: calculated for $C_{75}H_{22}O_8$ $(M)^+$, 1050.1315; found 1050.1365

4.2.8 Bis (carboxymethyl) 1,2-Methano[60]fullerene-61,61-dicarboxylate (11):

Compound **10** was dissolved in dichloromethane (2 mL) and trifluoroacetic acid (1 mL) was added. The reaction mixture was stirred for 16 h at room temperature. The progress of the reaction was monitored by TLC ($CHCl_3$/EtOH: 18/1). Upon completion, the reaction mass was diluted with water (10 mL) and dichloromethane (10 mL). The layers were separated and organic layer was washed with water (2x10 mL). Due to the formation of emulsion, THF was used for the extraction and evaporated to minimum volume and transferred to a watch glass for drying to yield the compound **(11).**

4.2.9 *tert*-Butyl 2-Mercapto ethyl Malonate (14):

To a mixture of 1M solution of mono *tert*-butyl malonate(0.1688g. 0.0010538 moles) and mercaptoethanol (0.09056g, 0.0011591 moles) in dry DCM, 1M solution of DCC (0.023699, 0.0011486 moles) was added. The reaction was stirred for 45 minutes. The progress of reaction was checked by TLC ($CHCl_3$). The byproduct was filtered off, the solvent was evaporated and the product was purified by column chromatography (Silica gel100; eluent: CHCl3) to give **14** as colourless oil. (0.063 g, 27%) ^{1}H NMR ($CDCl_3$, 300MHz): 1.42 (s, 9H), 1.51(t, 1H), 2.68 (m, 2H), 3.26 (s, 2H), 4.21 (t, 2H); ESI-TOF m/z: calculated for $C_9H_{16}O_4SNa$ $(M+Na)^+$, 243.0667; found 243.0679; calculated for $C_9H_{16}O_4SNaC_9H_{16}O_4S$ $(2M+Na)^+$, 463.1436; found 463.1455

4.2.10 2-(Acetylsulfanyl) ethyl *tert*-butyl Malonate (15):

To a mixture of compound **14** (0.0774g, 0.0003513 moles) and triethylamine(0.053317 g, 0.0005269 moles) in 2 mL of dry DCM in a sealed vial, acetyl chloride(25 µL, 0.0003513 moles) was added and reaction was stirred for 1h at room temperature. The progress of the reaction was monitored by TLC (hexane/ EtOAc: 7/3). The reaction was quenched by the addition of 5 mL of water. Reaction mixture was diluted with 20 mL of DCM and 20 mL of water and layers were separated. Organic layer was given one more washing with 20 mL of water, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The compound was purified by column chromatography (silica gel100; eluent: mixture of EtOAc in hexane) to get pure product of **(15)** as colourless oil. (0.078g, 85%) ^{1}H NMR ($CDCl_3$, 300MHz): 1.46 (s, 9H), 2.34 (s, 3H), 3.14 (t, 2H), 3.28 (s, 2H), 4.23 (t, 2H).

4.2.11 2-(Acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate (16):

Fullerene C_{60} (0.015 g, 0.0000208 moles) was dissolved in 110 mL of dry toluene under argon atmosphere. Iodine crystals (0.0052792 g, 0.0000208 moles) were added, followed by **15** (0.0054554 g, 0.0000208 moles) in 10 mL of toluene. The reaction mixture was covered with aluminum foil and DBU (0.00949 g, 0.0000624 moles) in 30 mL of toluene was added. The reaction mixture was stirred for 1 h at room temperature. The progress of the reaction was monitored by TLC (100% toluene system). The product was purified by column chromatography (silica gel 100, eluent: $CHCl_3$) and washed with pentane on a watch glass to yield **16** as dark brown solid (0.0125g, 61%). ^{1}H NMR ($CDCl_3$, 300MHz): 1.70 (s, 9H), 2.39 (s, 3H), 3.35 (t, 2H), 4.59 (t, 2H). ESI-TOF m/z: calculated for $C_{71}H_{16}O_5S$ $(M)^-$, 980.0718; found 980.0715; calculated for $C_{71}H_{16}O_5SCl$ $(M+Cl)^-$, 1015.0407; found 1015.0399

4.2.12 3-Bromo propyl ethyl malonate (18):

3-Bromopropanol (0.1846 g, 0.0013283 moles) was dissolved in 2 mL of dry DCM under argon atmosphere. The solution was cooled to 0°C and ethyl malonyl chloride **4** (0.2g, 0.0013283 moles) was added. The ice bath was removed and the reaction was stirred at room temperature for 48 hours. The progress of the reaction was monitored by TLC (Hexane/ EtOAc: 6/4). The solvent was evaporated under reduced pressure and purified by column chromatography (Silica gel 100, eluent: EtOAc in hexane) to yield compound **18** as colourless oil (0.2836g, 84%). ^{1}H NMR ($CDCl_3$, 300MHz): 1.27 (t, 3H), 2.19 (m, 2H), 3.37 (s, 2H), 3.46 (t, 2H), 4.18 (q, 2H), 4.29(t, 2H).

4.2.13 [3-(acetylsulfanyl) propyl] ethyl malonate (19):

Potassium thioacetate (0.018 g, 0.000158 moles) and compound 18 (0.020 g, 0.000079 moles) were dissolved in 3 mL of acetone (dried over P_2O_5) under argon atmosphere in a sealed vial. The reaction mass was heated to 50°C for 4 hours on a heating block. The

progress of the reaction was monitored by TLC (Hexane/ EtOAc: 7/3). The byproduct was filtered off; the solvent was evaporated under reduced pressure. The target compound was purified by column chromatography (Silica gel 100, eluent: mixture of EtOAc in hexane) to give **19** as colourless oil (0.0143g, 73%). ^{1}H NMR ($CDCl_3$, 300MHz): 1.28 (t, 3H), 1.93 (m, 2H), 2.33 (s, 3H), 2.93 (t, 2H), 3.38 (s, 2H), 4.19 (m, 4H).

4.2.14 3-(Acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate (20):

Fullerene C_{60} (0.020 g, 0.0000277 moles) was dissolved in 110 mL of dry toluene under argon atmosphere. Iodine crystals (0.0070305 g, 0.0000277 moles) were added, followed by **19** (0.0068776g, 0.0000277 moles) in 10 mL of toluene. The reaction mixture was covered with aluminum foil and DBU (0.01265 g, 0.0000831 moles) in 30 mL of toluene was added. The reaction mixture was stirred for 1 hour at room temperature. The progress of the reaction was monitored by TLC (100% toluene system). The product was purified by column chromatography (silica gel 100, eluent: $CHCl_3$), dried on a watch glass and washed with pentane to yield **20** as dark brown solid. 0.0147g (55% yield) ^{1}H NMR ($CDCl_3$, 300MHz): 1.49 (t, 3H), 2.14 (m, 2H), 2.37 (s, 2H), 3.06 (t, 2H), 4.56 (m, 4H). ESI-TOF m/z: calculated for $C_{70}H_{14}O_5S$ (M)+, 967.0640; found 967.0630

4.2.15 C_{60}-disulfide adduct (21):

Fullerene C_{60} (0.0291 g, 0.0000404 moles) was dissolved in 110 mL of dry toluene under argon atmosphere. Iodine crystals (0.0102 g, 0.0000404 moles) were added to the reaction mass followed by compound **14** (0.0089g, 0.0000404 moles) in 10 mL of toluene. The reaction mixture was covered with aluminum foil and DBU (0.01845 g, 0.00012121 moles) in 30 mL of toluene was added. The reaction mixture was stirred for 1 hour at room temperature. The progress of the reaction was monitored by TLC (100% toluene system). The product was purified by column chromatography (silica gel 100, eluent: $CHCl_3$) to yield **21** as dark brown solid. ESI-TOF m/z: calculated for $C_{78}H_{26}O_8S_2$ $(M)^+$, 1154.1069; found 1154.1057.

4.2.16 Ethyl (3-Sulfanyl propyl) 1, 2-Methano [60] fullerene-61, 61-dicarboxylate (22):

Compound **20** (0.0147g, 0.000152 moles) was dissolved in a mixture of 7.87 mL of DCM (dried over K_2CO_3) and 0.5216 mL of dry methanol (HPLC grade) in a sealed tube equipped with argon balloon. The contents were cooled to 0°C and acetyl chloride (372 µL, 0.005244 moles) was added into it. The ice bath was removed and the r.m. was stirred for 5 hours at room temperature. The progress of the reaction was monitored by TLC (100% DCM). The reaction mixture was diluted with 30 mL of DCM and the organic layer was washed with 30 mL of water 5 times to remove the

acid. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The target compound was purified by column chromatography (silica gel 60, eluent: 1:1 mixture of DCM in hexane). The fraction collected was concentrated to minimum volume, dried out on a watch glass and washed with pentane to get dark brown solid of **22** (0.0091g, 65%). ^{1}H NMR ($CDCl_3$, 300MHz): 1.50 (m, 4H), 2.16 (m,2H), 2.72 (q, 2H), 4.58 (m, 4H). ESI-TOF m/z: calculated for $C_{68}H_{12}O_4S$ $(M)^+$, 925.0535; found 925.0543.

5 CONCLUSION

We have synthesized fullerenes with anchors such as mono- and bis- carboxy, thioacetate, and thiol functional groups. The process involves multi-step synthetic schemes. In order to minimize the loss of the expensive fullerene molecule, all the linkers were synthesized separately. The anchors were shielded by suitable protecting groups before attaching to the fullerene core by Bingel reaction. Later the protecting groups were cleaved to expose the anchors for surface modification. Bingel reaction of unprotected thiol with fullerene is particularly interesting as it produced bis-adduct with a disulphide bond. The list of modified fullerenes with different anchoring groups encircled are shown in Figure 4.1

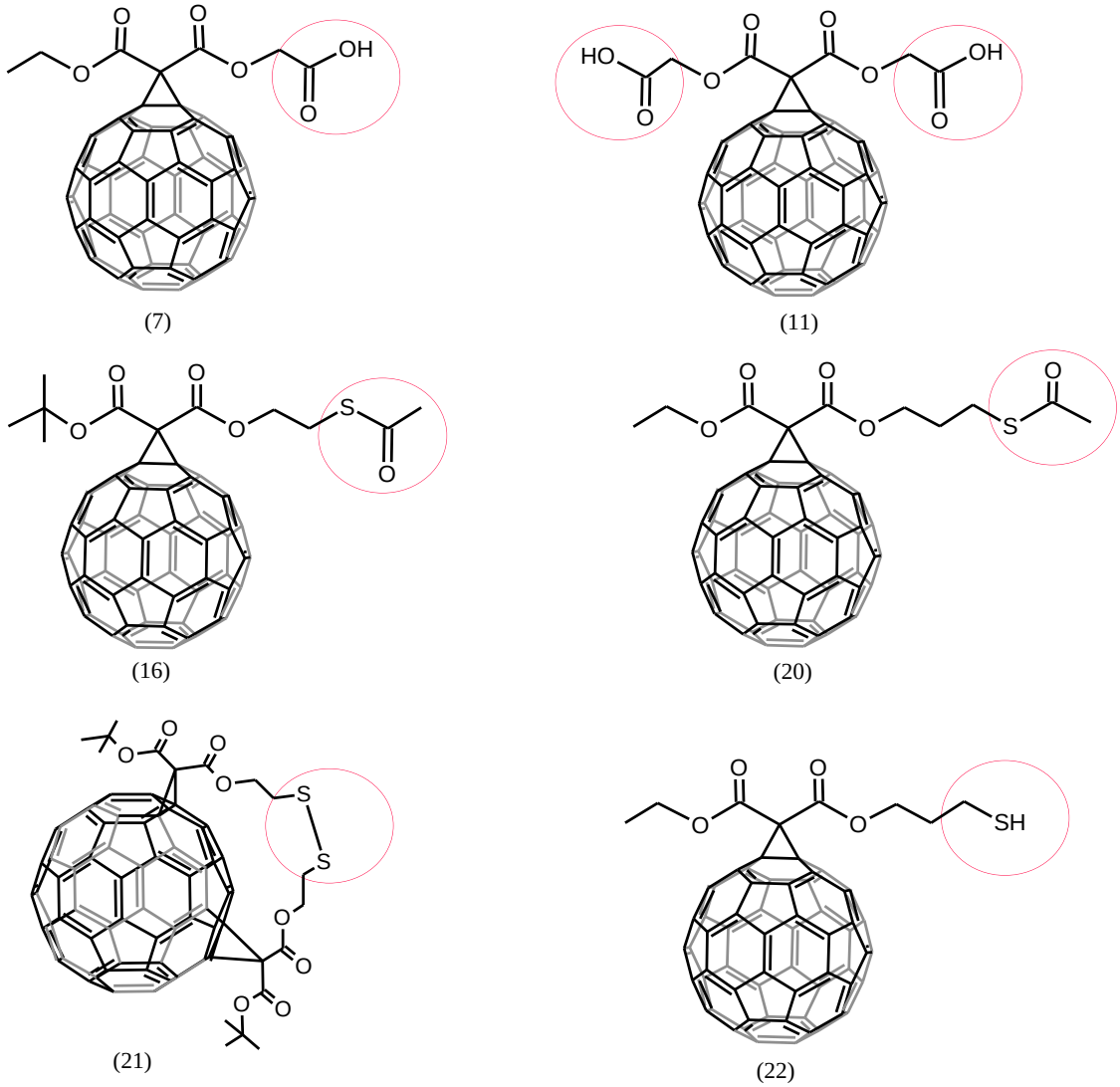


Figure 4.1: List of modified fullerenes with anchors synthesized during the work

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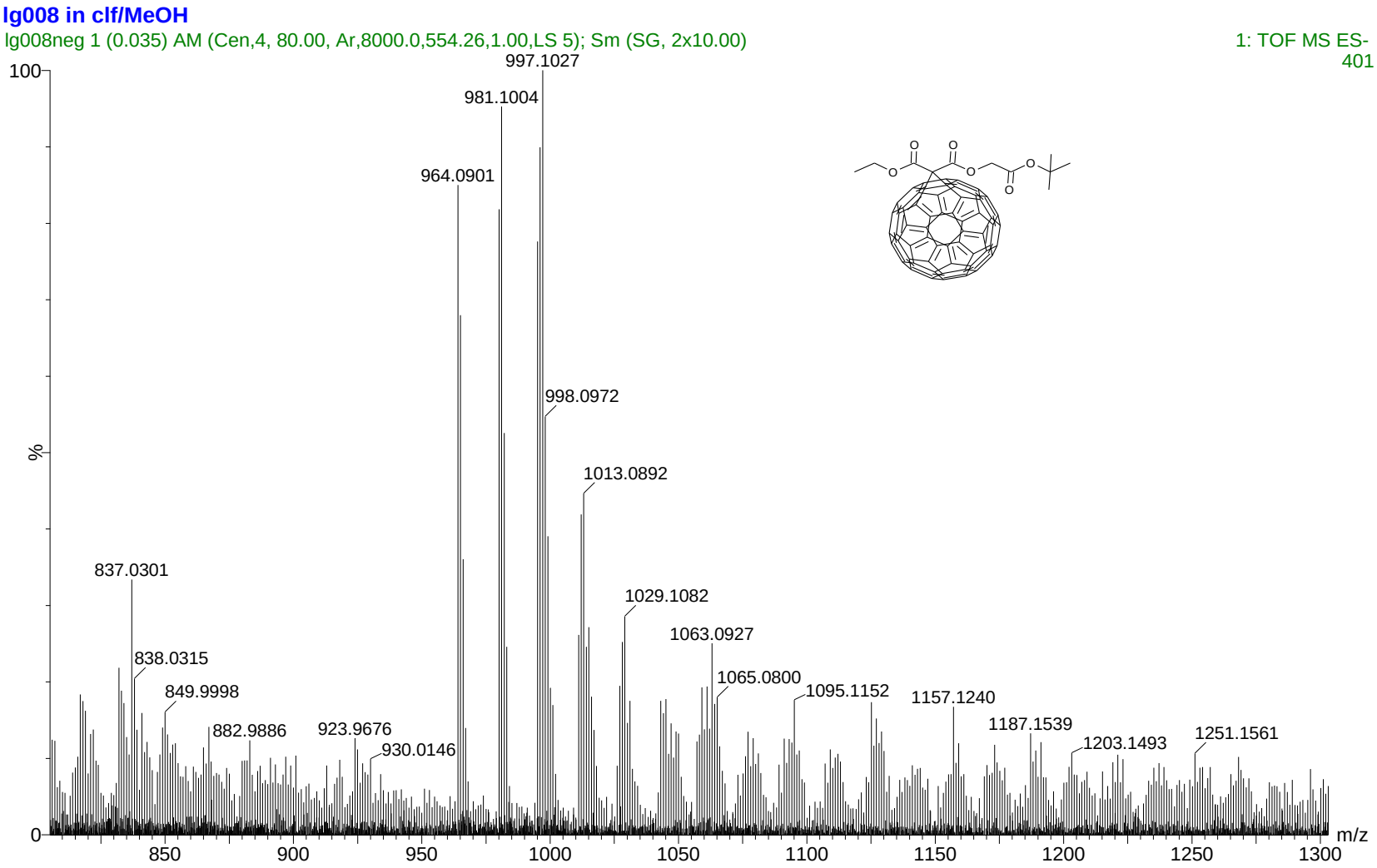
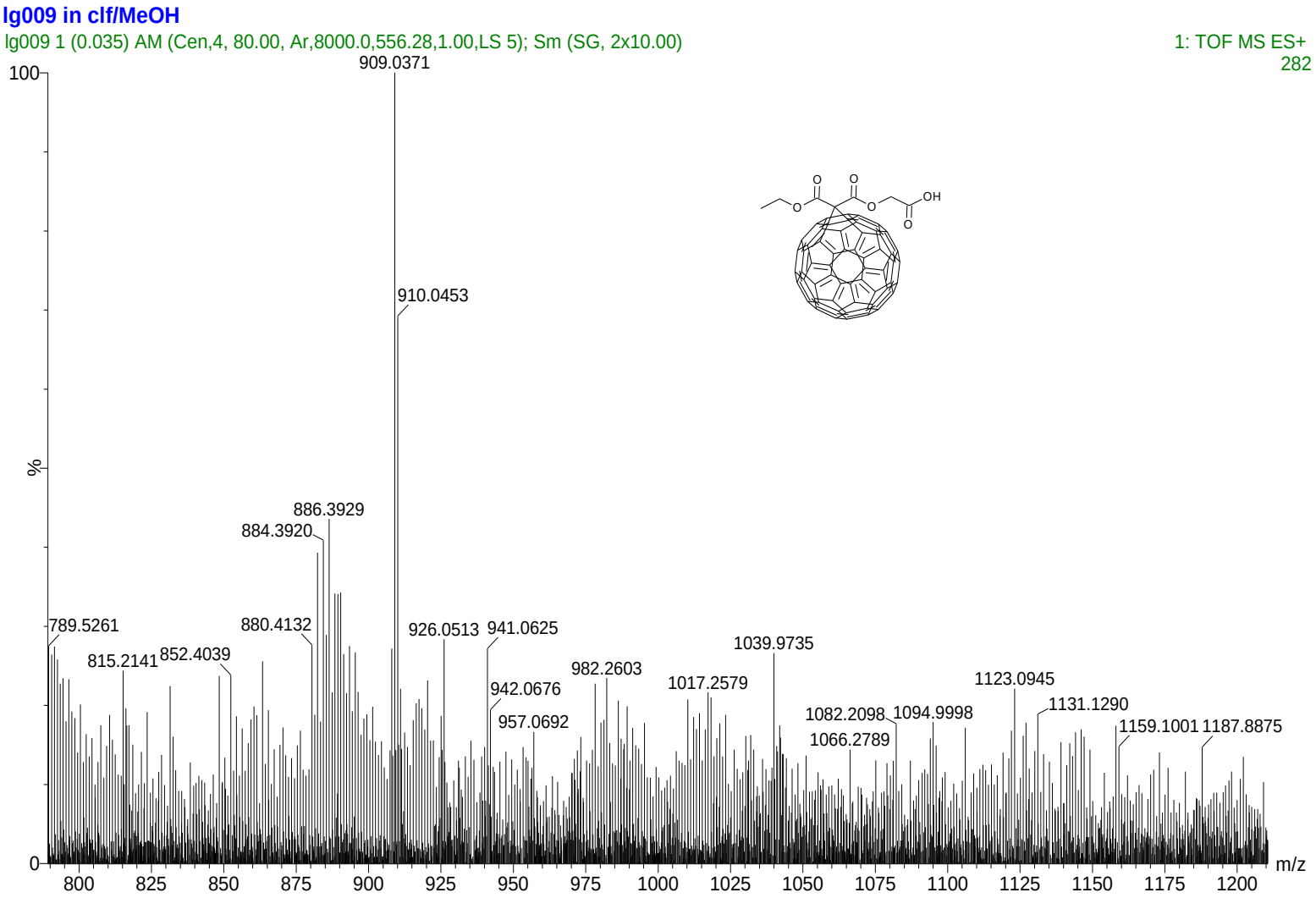
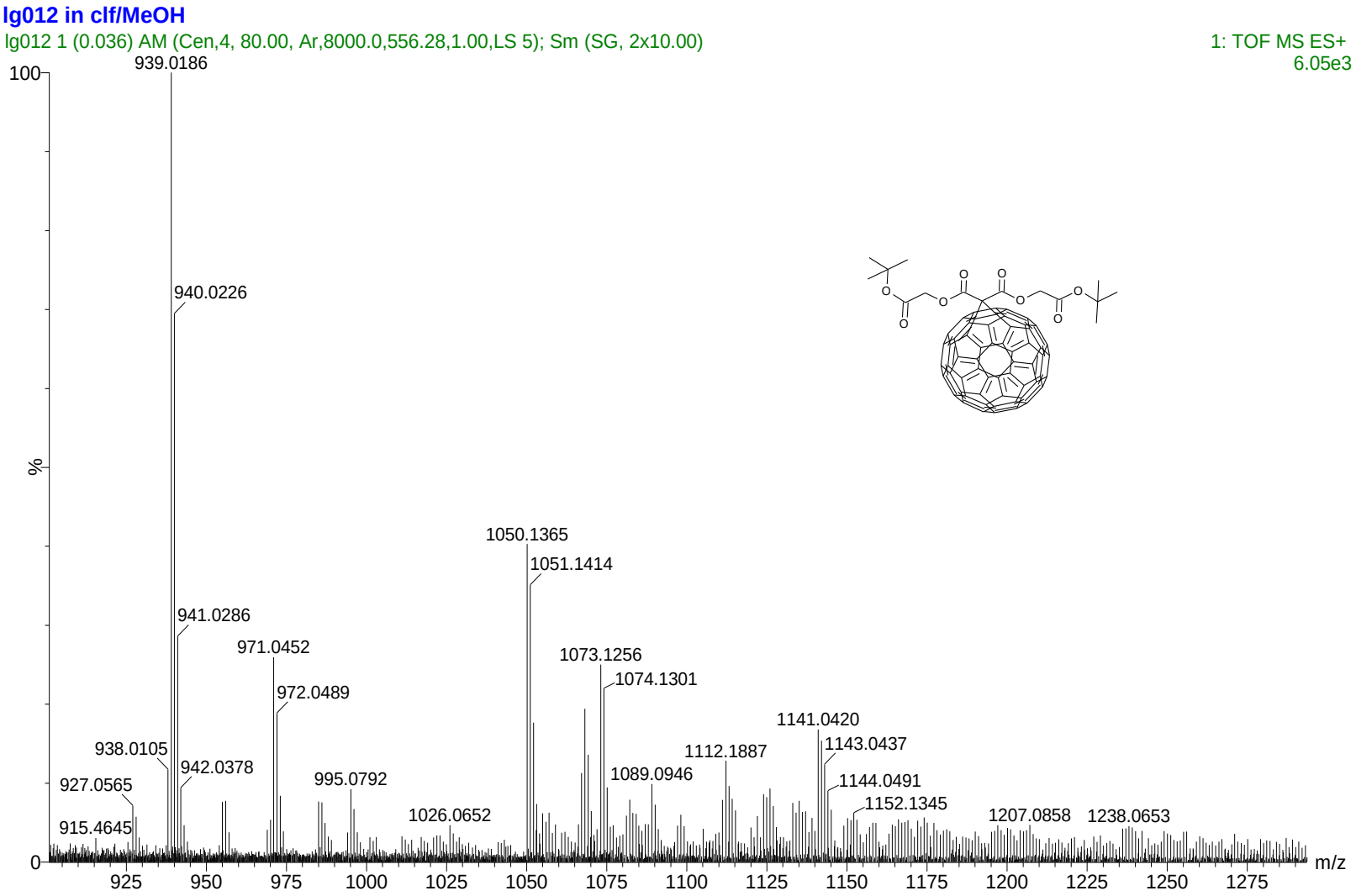


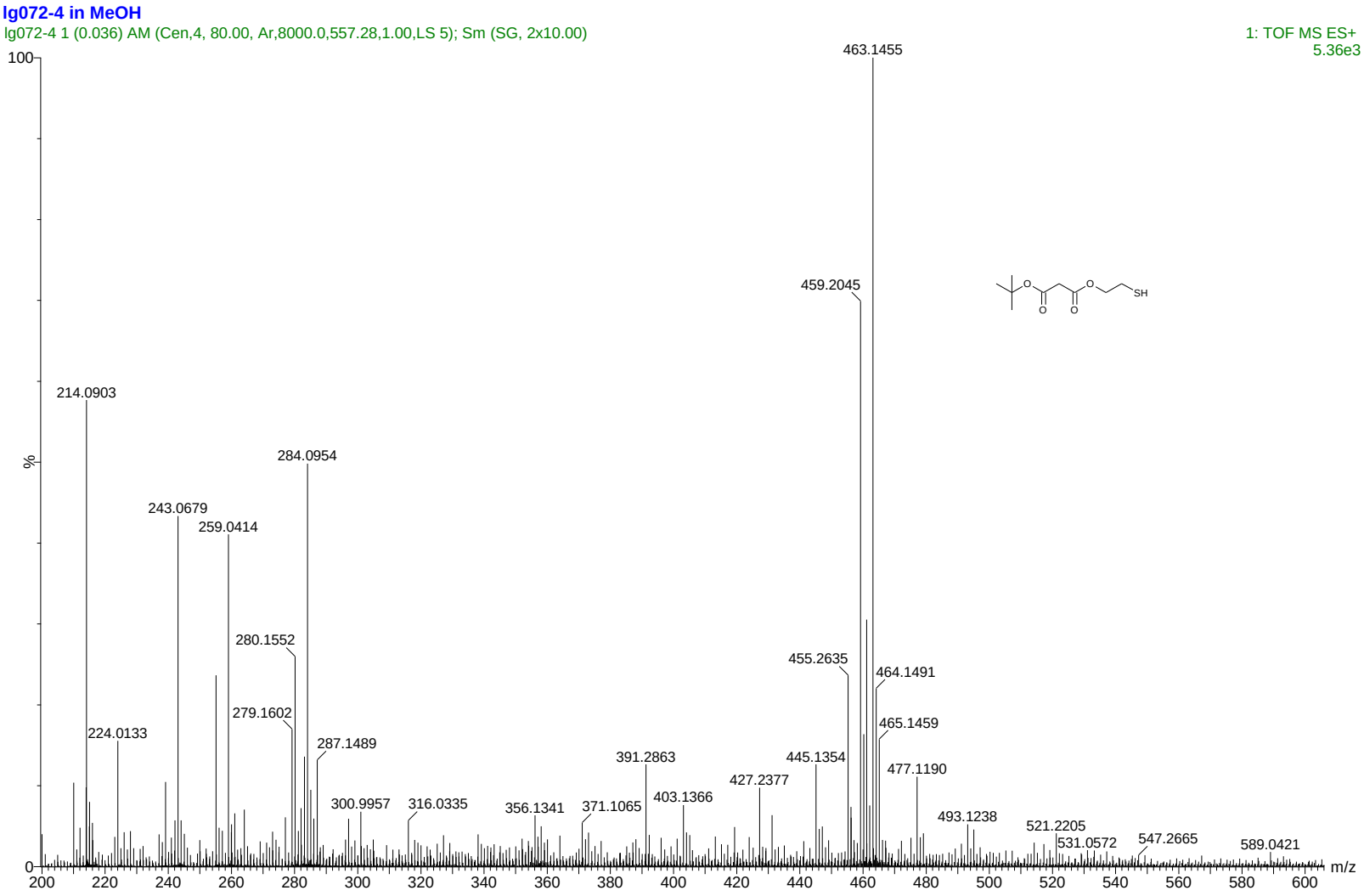
APPENDIX 1: Mass spectrum of 2-(*tert*- Butoxy)-2-oxoethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate



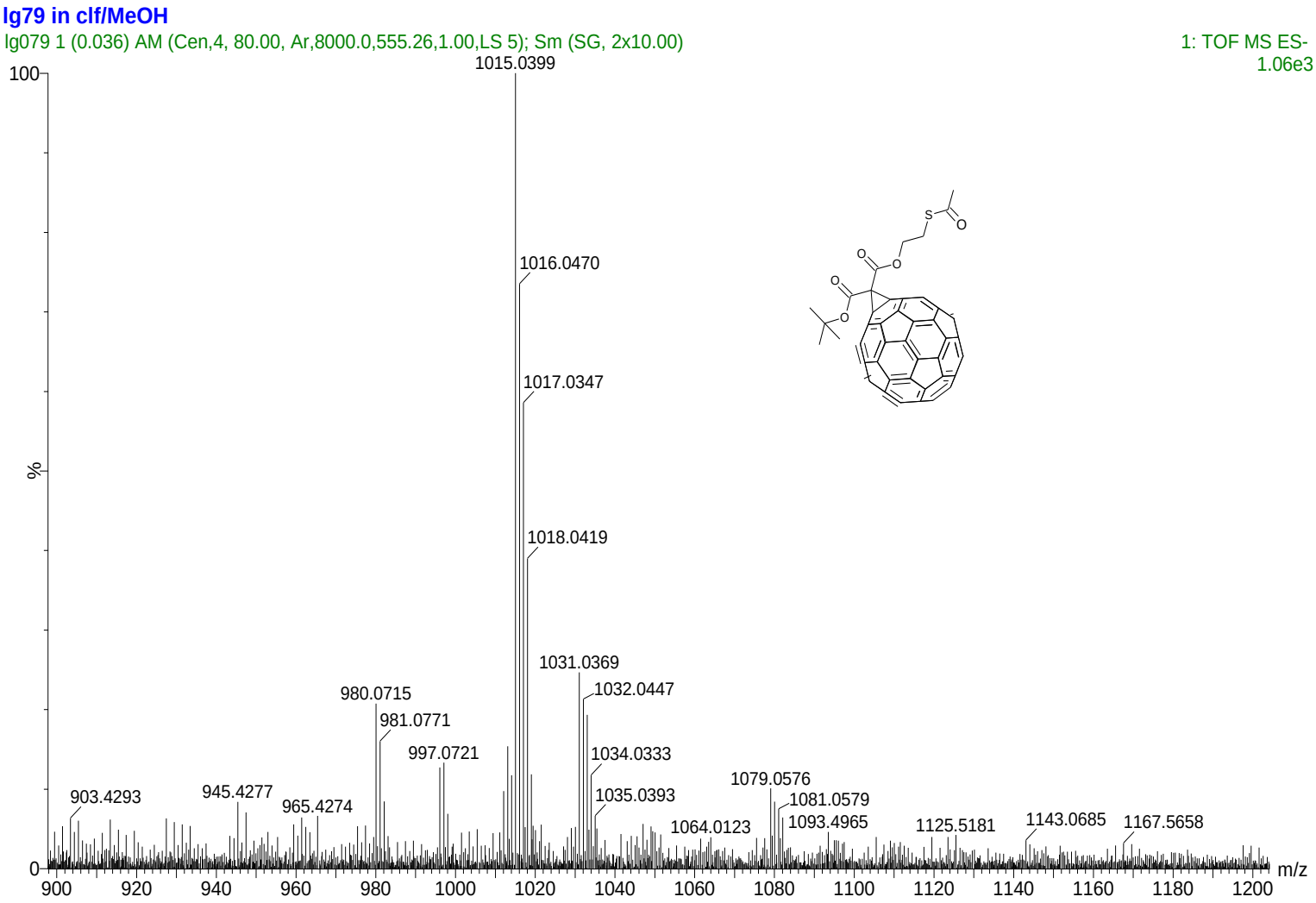
APPENDIX 2: Mass spectrum of Carboxymethyl ethyl 1, 2-Methano [60] fullerene-61, 61-dicarboxylate



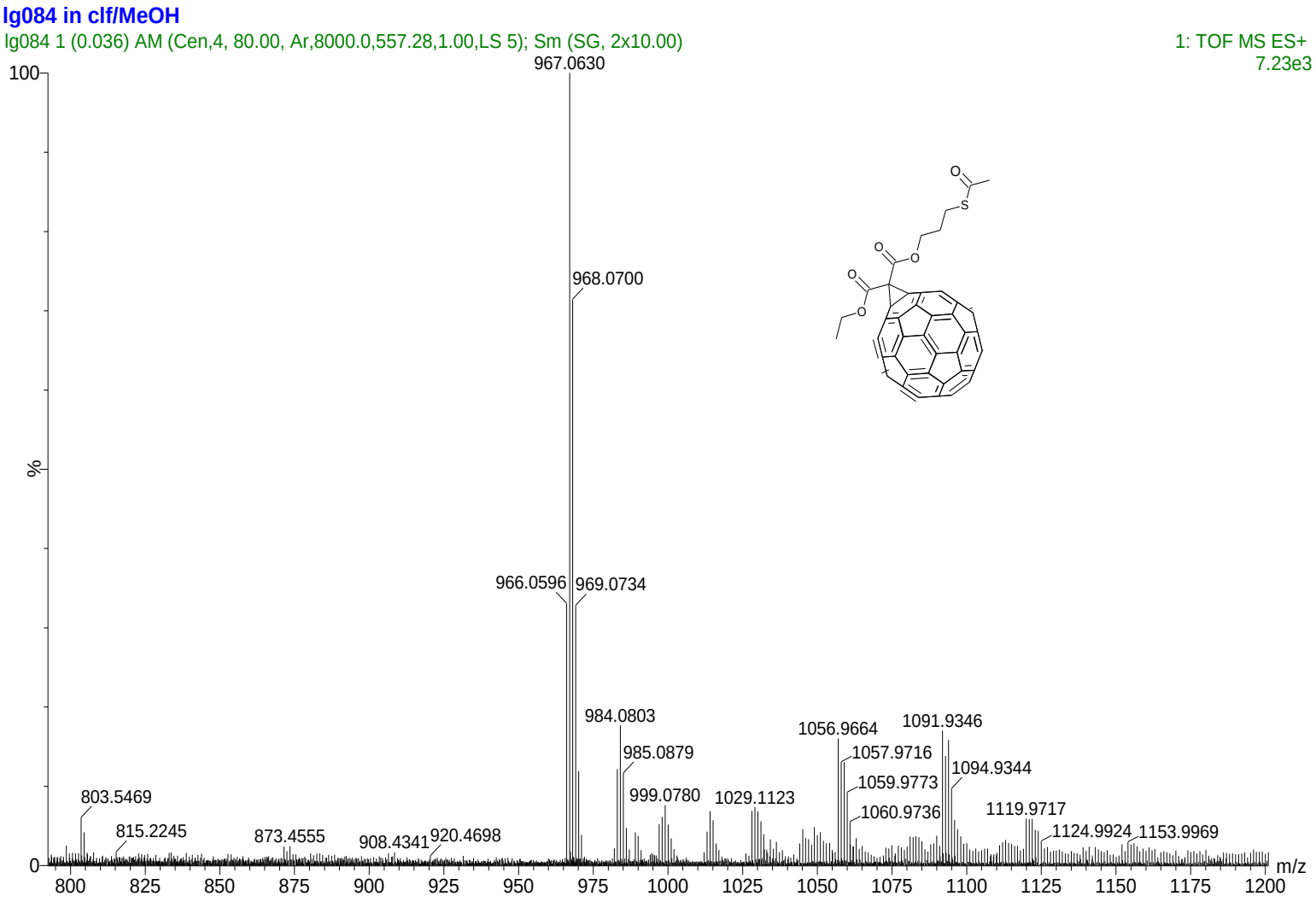
APPENDIX 3: Mass spectrum of Bis [2- (*tert*- butoxy-2-oxoethyl)] 1, 2-Methano [60] fullerene-61, 61-dicarboxylate



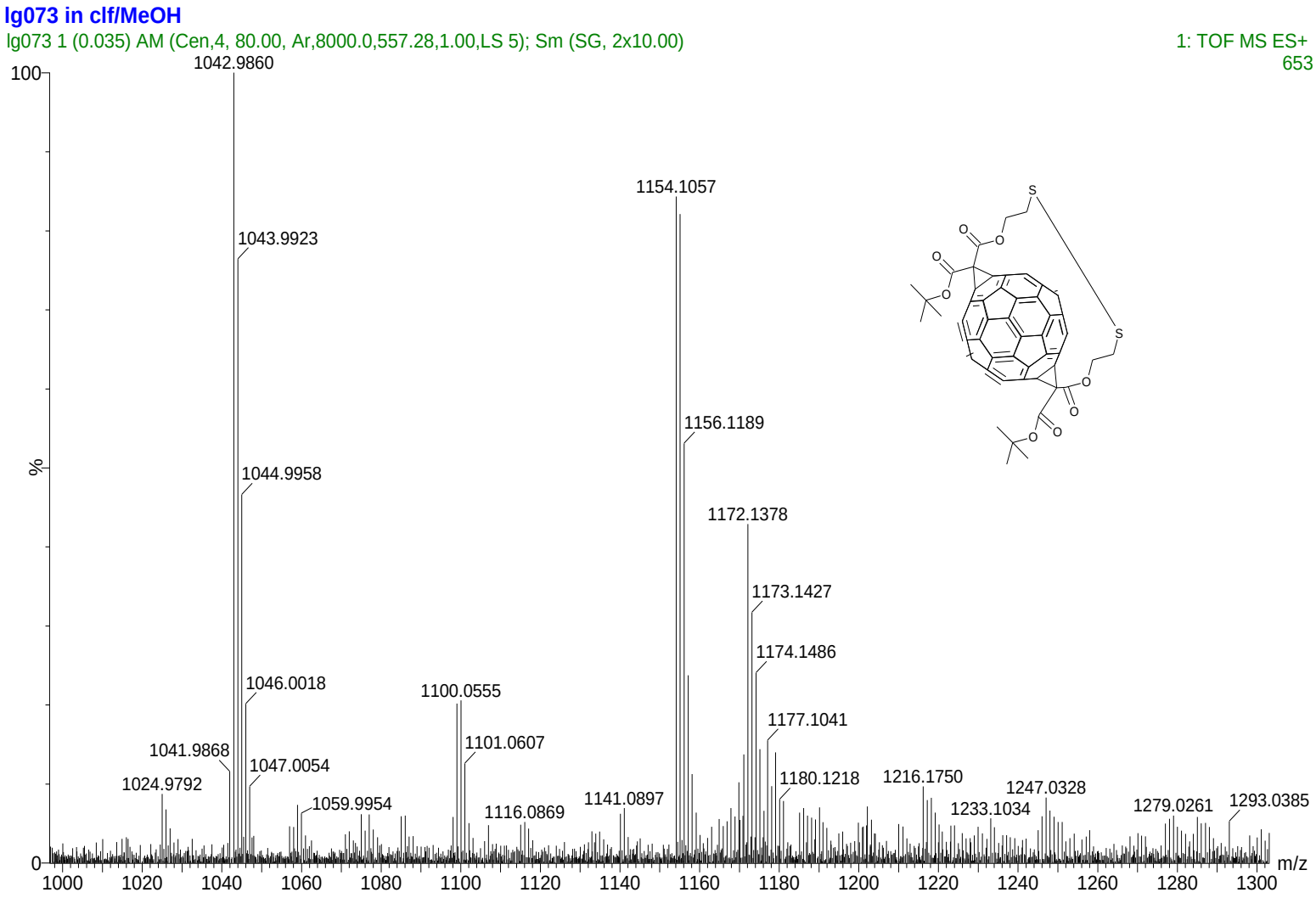
APPENDIX 4: Mass spectrum of *tert*-Butyl 2-Mercapto ethyl Malonate



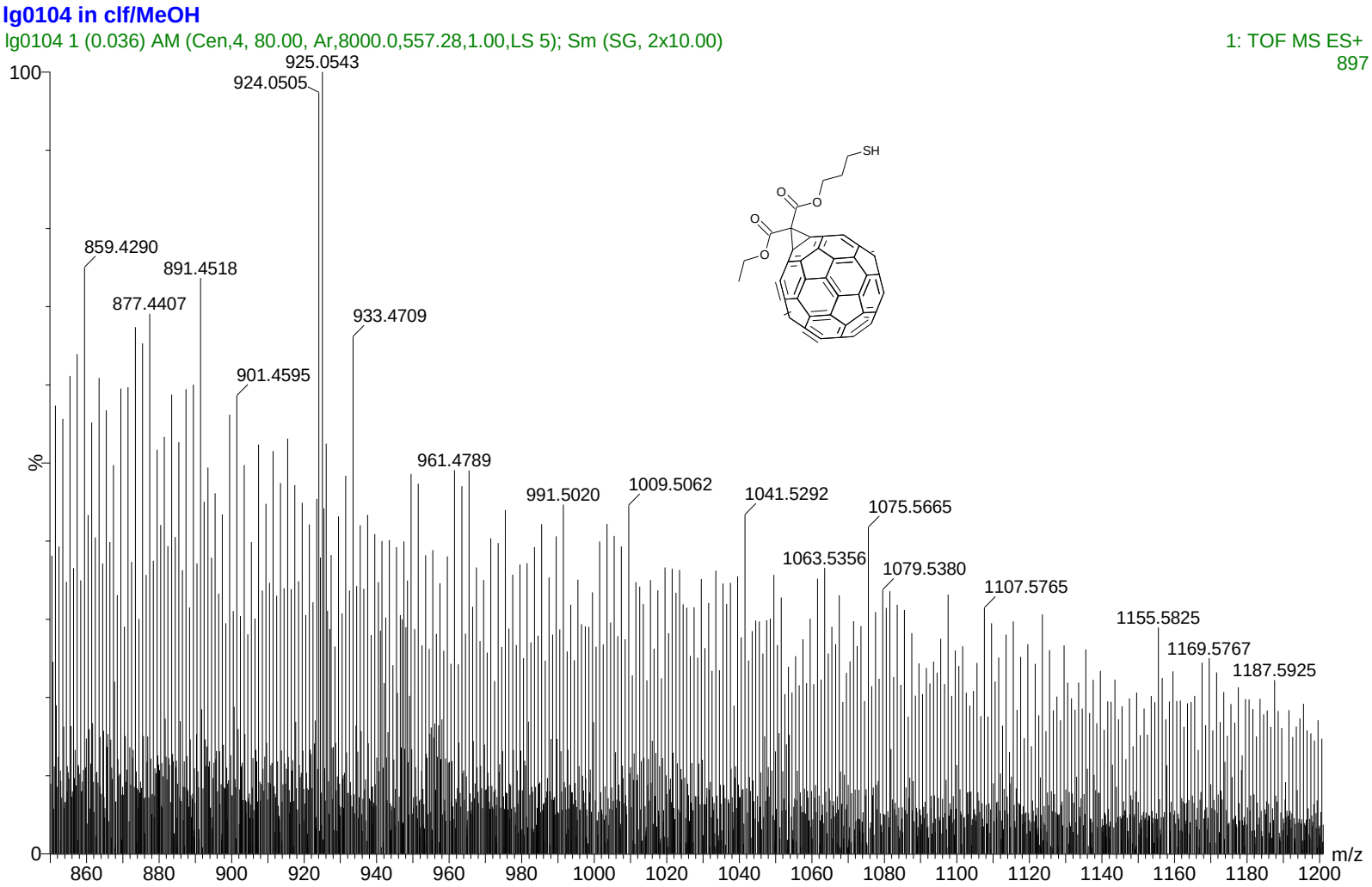
APPENDIX 5: Mass spectrum of 2-(Acetylsulfanyl) ethyl *tert*-butyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate



APPENDIX 6: Mass spectrum of 3-(Acetylsulfanyl) propyl ethyl 1, 2-methano [60] fullerene-61, 61-dicarboxylate



APPENDIX 7: Mass spectrum of C_{60}-disulfide adduct



APPENDIX 8: Mass spectrum of Ethyl (3-Sulfanyl propyl) 1, 2-Methano [60] fullerene-61, 61-dicarboxylate